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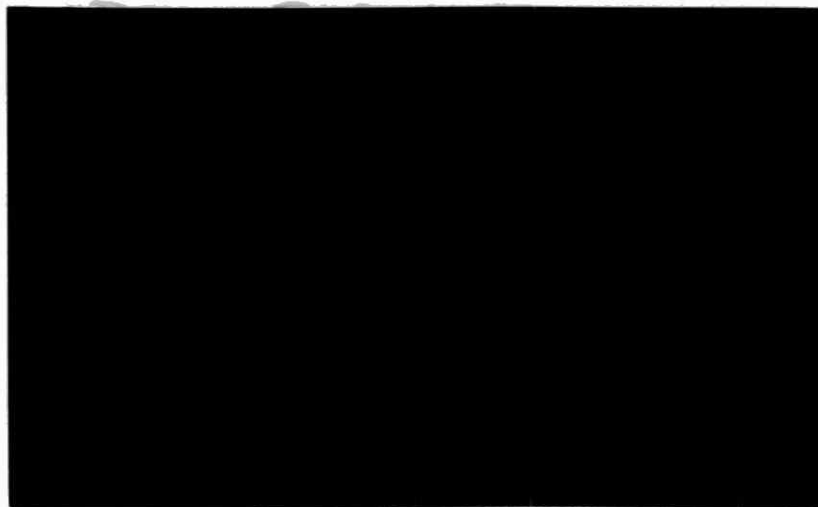
RESEARCH AND TECHNOLOGY BRANCH

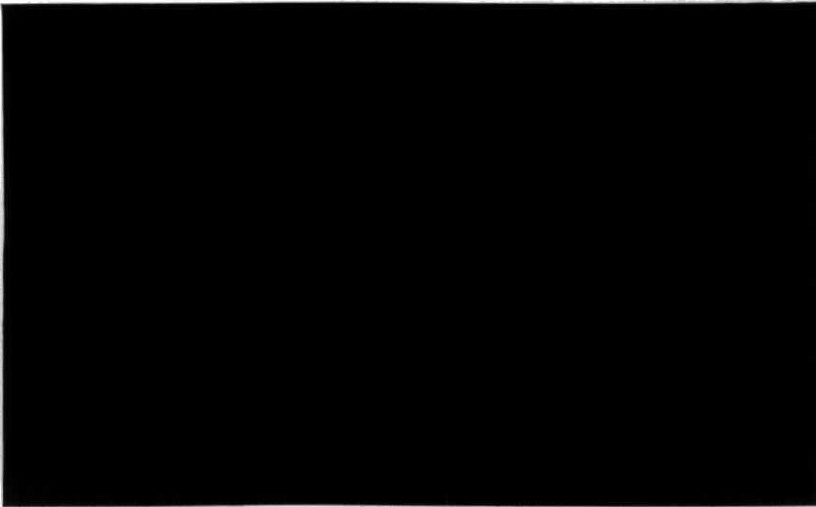


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Availability of zinc to benthic
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AVAILABILITY OF ZINC
TO BENTHIC ORGANISMS FROM
SEDIMENT FRACTIONS

RAC PROJECT: 277RR

OCTOBER, 1988

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AVAILABILITY OF ZINC TO BENTHIC ORGANISMS FROM SEDIMENT FRACTIONS

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ABSTRACT

A novel radiolabelling technique was used to identify the sediment chemical fraction(s) serving as a source of zinc to tubificid worms in Toronto Harbour sediments. Two species of tubificids, Tubifex tubifex and Limnodrilus hoffmeisteri, were grown for one and two months on sediments labelled with zinc-65. When subjected to chemical fractionation using the Tessier technique, the specific activity of each fraction (activity zinc-65: total zinc) was compared with that of the worms. The specific activity of the worms was closest to that of the Fe/Mn oxide-bound zinc, a fact suggesting that the worms are assimilating zinc from this fraction. Based on the vertical distribution of chemical fractions of zinc in Toronto Harbour cores, 50 to 70% of sediment-bound zinc is available to tubificids.

Separate labelling experiments showed that when added to the sediments inorganic zinc is rapidly taken up by the particulate fraction (within three minutes). A meta-stable equilibrium is established where each chemical fraction accumulates a different proportion of the metal. The bioavailability of a metal introduced into aquatic sediments will depend on its distribution between the sediment fractions. In a metal - metal radioisotope system such as zinc-zinc-65, the specific activity of a bioavailable sediment fraction indicates the increase in exposure of an organism to small additions of metal to the sediments.

Autoradiographic analysis of tissue sections from tubificids exposed to lead-210 in water and sediments showed that in both cases lead is accumulated in identical sites in the worms. Much of the lead accumulates in nephridia where it is presumably prepared for excretion. Soluble lead-210 was much more available to the worms than particulate - bound lead-210, a fact also suggested in the zinc-65 experiments. Accumulations of lead-210 in the coelomic cavity of the anterior and posterior segments of some worm sections suggested that soluble lead is taken up through the epidermis in these segments. The mechanism of uptake of particulate-bound metals remains uncertain.

1.0 INTRODUCTION

Zinc of industrial origin is substantially elevated in recently deposited sediments of the nearshore zone of the Great Lakes (Fitchko and Hutchinson, 1975; Konasewich *et al.*, 1978; Persaud *et al.*, 1985), as well as lakes in southern Ontario (Evans *et al.*, 1983). The toxicity of zinc to aquatic biota is well documented (Brungs, 1969; Spehar, 1976; Chapman, 1978; Pierson, 1981; Anderson *et al.*, 1980; Brkovic-Popovic and Popovic, 1977; Forstner and Wittmann, 1981; Attar and Maly, 1982). Since benthic deposit-feeders are known to accumulate zinc and other heavy metals from ingestion of sediment (Luoma and Jenne, 1976; Bryan and Hummerstone, 1978; Luoma, 1983), it is of considerable importance to determine how much of this recently deposited zinc can be assimilated by benthic organisms and transferred to fish and other organisms higher in the food chain.

Availability of trace metals to benthic deposit-feeders is intimately dependent upon the physical-chemical forms in which the metals are present in the sediments (Luoma and Jenne, 1976a, b; Bryan and Hummerstone, 1977; Bryan and Uysal, 1978; Luoma and Bryan, 1978; Luoma, 1983; Tessier *et al.*, 1984). The accumulation of these metals by benthic organisms is only poorly predicted from their total concentration in the sediments (Bryan and Hummerstone, 1977). In most studies, attempts have been made to correlate the heavy metal contents of deposit-feeding macrofauna with a particular chemical fraction or fractions of the metal in the sediments. The ultimate goal of these studies is to find a universal predictor of the metal content of benthic invertebrates. Thus, Luoma and Bryan (1978) related the lead content of the bivalve *Scrobicularia* in a British estuary to the ratio of Pb/Fe in the sediments extracted with 0.1 N HCl. This weak acidic extract was supposed to resemble the gut environment. Iron was hypothesized to control biological availability by either competing in the gut with Pb for binding sites or, as amorphous iron oxides, by binding with Pb in the sediments and decreasing its bioavailability. Luoma and Jenne (1976a, b) labelled natural and artificial sediments with heavy metal radioisotopes and found good correlations between uptake of zinc-65 and cadmium-109 in the deposit-feeder *Macoma balthica* with readily-exchangeable zinc-65 and ethanol-extracted cadmium-109 respectively in the sediments. Uptake from organic detritus was very low. Luoma and Bryan (1979) related the zinc content of the bivalve *Scrobicularia* to easily-exchangeable zinc in the sediments. In the same study, the zinc content of the bivalve *Macoma balthica* from San Francisco Bay was related to the ratio of oxide-bound iron divided by easily exchangeable manganese and organic carbon in the sediments.

Tessier et al. (1984) related the copper concentration in the bivalve Elliptio (actually a filter feeder) to the ratio of Cu (exchangeable + carbonate-bound + Fe/Mn oxide-bound) to oxide-bound iron in freshwater sediments.

The latter studies reveal some of the problems, common to all correlations, that have arisen in applying the correlation technique. Chemical fractions of metals in sediments, especially within a restricted geographical area are often intercorrelated (Tessier et al., 1984) and a particular correlation between a chemical fraction and the body burden of a benthic invertebrate may not reflect a cause-and effect relation. While this objection may not be important from the perspective of managing heavy metal pollution in a particular study area, the correlation obtained may only apply to this one sampling area. In fact, many of the correlations found to date do appear to be site specific. The zinc content of bivalves at the two sites studied by Luoma and Bryan (1979) and discussed above were best predicated by very different chemical ratios. As more and more studies are conducted, the number of significant correlations has increased proportionally. In addition many of these correlations, such as those found by Luoma and Bryan (1979) and Tessier et al., (1984), are cumbersome ratios involving multiple fractions and metals. The correlation technique, therefore, has failed to produce the long-sought universal predictor (if such exists) of heavy metal contents of benthic deposit-feeders.

In this study we present an alternative method for determining the bioavailability of heavy metals in aquatic sediments that involves labelling sediments with a heavy metal radionuclide. When a benthic deposit-feeder feeds on sediments containing a heavy metal and analogous radioisotope, the specific activity of the radioisotope in the organism should approach the specific activity of the radioisotope in the biologically available fraction(s) of the sediments (Ophel, 1965; Ophel and Fraser, 1971). In this context, specific activity is defined as the ratio of the activity of the heavy metal radionuclide per gram of sediment (or organism) to the total concentration of the heavy metal per gram of sediment (or organism). Measurements of the specific activity in the organisms and in chemical fractions of the sediment, therefore, replace correlations between total body content and concentration in each chemical fraction as a method of determining which fraction serves as a source of the metal to the organisms.

Specific activity has been used in other studies to trace the movement of heavy metals in biological systems. Duke et al. (1966) added zinc-65 to estuarine ponds and traced the movement of the isotope in the water, sediments and fauna.

By examining the specific activity, defined as above, they were able to demonstrate that the sediments controlled the cycling of zinc in the water and fauna. Most of the sediment-bound zinc was contained in a fraction which exchanged very slowly with the water above, while a small part of the zinc was found in fractions having a rapid turnover rate and exchanging rapidly with the water and fauna. Cross et al. (1971) examined specific activities of zinc-65 in water and particulates in experimental marine systems and found that equilibrium of zinc between these two fractions had not been reached after nine months. Renfro et al. (1975) examined specific activities of zinc-65 in marine organisms exposed to this isotope and found evidence for pools of zinc within adult organisms that exchange very slowly, if at all, with zinc available in their food or surrounding water. Andrews et al. (1985), comparing the specific activity of cobalt-60 in sediment-chemical fractions with the specific activity of cobalt-60 in tubificid worms grown on these sediments, concluded that the easily-exchangeable cobalt fraction was the most probable source of this metal to the worms. Significantly, organically-bound cobalt was not available to the worms. These results explained the rather low uptake rates of cobalt by the natural fauna of the Ottawa River and by the Tubifex worms, since a large proportion of the metal was in a residual fraction and presumably unavailable to benthic organisms.

Measurements of specific activity can also be used to trace the movement of recently introduced metal through potentially bioavailable sediment fractions. This work follows that of Andrews et al. (1985) who found that cobalt-60 was taken up initially and retained for months in the easily exchangeable and carbonate-bound fractions and was probably highly available to deposit-feeders. On the other hand, routine fractionation of the sediments indicated that over 80% of the total cobalt in these sediments was in a residual or oxide-bound fraction, presumably unavailable to deposit-feeders. There was, therefore, a non-proportional distribution of the newly added cobalt between the chemical fractions of this metal in the sediments. The bioavailability of recently incorporated cobalt was substantially greater than that of "aged" and "reworked" cobalt found in surface sediments.

This report describes a study of the bioavailability of zinc to benthic deposit-feeders in Toronto Waterfront sediments by using zinc-65 and the radiolabelling technique of Andrews et al. (1985).

The objectives of this study were as follows:

1. to identify the sediment chemical fraction(s) serving as a source of zinc to benthic deposit-feeders,
2. to examine the vertical distribution of this/these sediment fractions in the sediments in relation to animal feeding behaviour,
3. to compare the bioavailability of zinc recently incorporated in the sediment with that of "aged" zinc measured in routine sediment fractionation of near-surface sediments, and
4. to re-examine MOE data with the aim of generating a predictive relationship between zinc in sediment chemical fractions and zinc in the bodies of benthic deposit-feeders.

Based on some of the results of this study, an additional study was conducted to determine by autoradiography the mechanism of heavy metal uptake by oligochaetes in sediments.

2.0 METHODS

2.1 Source of Sediment-bound Zinc to Benthic Deposit-Feeders

To determine which chemical fraction of the sediments serves as the source of zinc to benthic deposit-feeders, two species of oligochaetes, Tubifex tubifex and Limnodrilus hoffmeisteri were grown on Toronto Harbour sediments labelled with zinc-65. The activity and specific activity of zinc-65 in the organisms were then compared with those in chemical fractions of the sediments.

Three litres of surface sediments were collected from a selected station in Toronto Harbour by Ekman dredge (Figure 1). Thirty microcuries of inorganic zinc-65 were added to these sediments and allowed to equilibrate for three weeks. The sediments were continually stirred during this time to maintain oxic conditions. About 150 ml of this sediment were then added to each of 22 crystallizing dishes and covered with 2 cm of dechlorinated tap water.

Oligochaete worms were collected from Keating Channel in Toronto Harbour by sieving sediments taken by an Ekman dredge through a 250 um mesh net. Two species of worm predominated in these sediments, Tubifex tubifex and Limnodrilus hoffmeisteri, in the approximate ratio of 6:1. These animals were then grown for five weeks on sediments of relatively low zinc concentrations from Bowmanville Harbour (Thomas and Mudroch, 1979). This procedure was followed to ensure a large supply of worms having a relatively low zinc content.

Ninety tubificids from the Bowmanville Harbour sediments were then placed in each of the crystallizing dishes containing labelled Toronto Harbour sediments. Twelve dishes were devoted to Tubifex while eight were devoted to Limnodrilus. Two additional dishes of sediments were maintained as controls without animals (Table 1). When added to the dishes, both species of tubificids quickly burrowed into the sediments and appeared to feed normally. Within 24 hours, worm castings were evident on the sediment surface. The sediments were stirred about every week to prevent anoxia and the associated diagenetic changes. All worm incubations were conducted at 9°C.

FIGURE 1:
LOCATION OF SAMPLING STATIONS IN TORONTO HARBOUR.

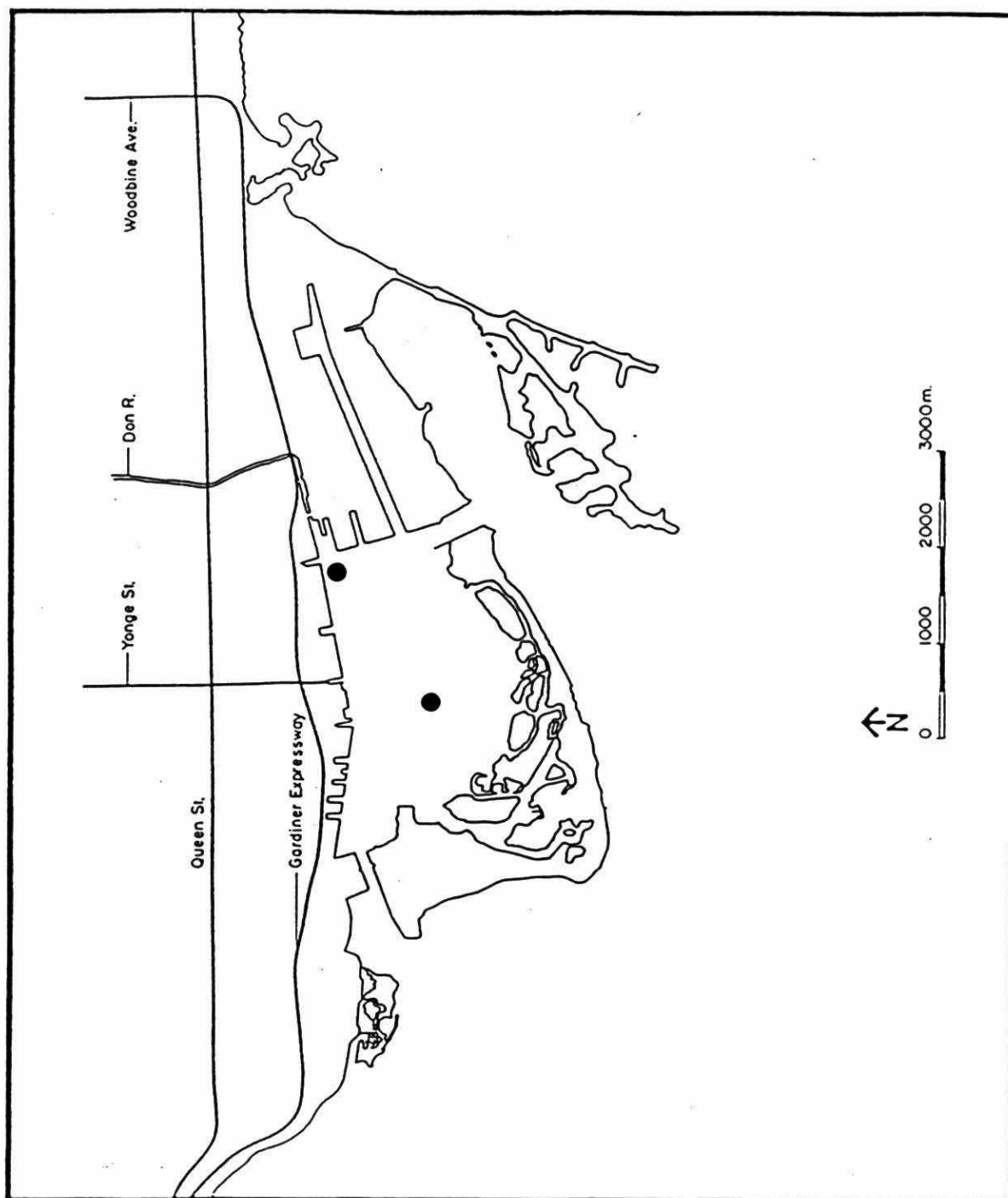


TABLE 1: DISTRIBUTION OF TWO OLIGOCHAETE SPECIES IN EXPERIMENTAL DISHES OF LABELLED TORONTO HARBOUR SEDIMENTS AND DURATION OF THE EXPERIMENT

Dish No.	Species		Duration (months)
	<u>Tubifex</u> <u>tubifex</u>	<u>Limnodrilus</u> sp.	
1	-	+	1
2	-	+	1
3	-	+	1
4	-	+	1
5	+	-	1
6	+	-	1
7	+	-	2
8	+	-	2
9	+	-	1
10	+	-	1
11	+	-	1
12	+	-	1
13	-	+	2
14	-	+	2
15	-	+	2
16	-	+	2
17	+	-	2
18	+	-	2
19	+	-	2
20	+	-	2
21 (control)	-	-	1
22 (control)	-	-	2

Ten experimental dishes were sampled at one- and two-month intervals (Table 1) at which time two samples of the supernatant water, two sediment samples (5 gm) and all the worms were taken from each dish.

The sediment samples were subjected to a modified version of the sequential extraction procedure of Tessier et al. (1979) and the sediment-bound zinc was separated into the operationally defined categories of:

- o interstitial zinc,
- o easily-exchangeable zinc,
- o carbonate-bound zinc,
- o Fe/Mn oxide-bound zinc,
- o organically-bound, and
- o residual zinc.

Separate samples were also taken for total zinc. In all cases, the samples were treated wet rather than dry and ground, as the latter processes dramatically change the metal partitioning (Chen et al., 1976; P. Campbell, pers. comm.). Total and residual zinc were analyzed by digesting the sediments in nitric acid at 95°C, rather than hydrofluoric acid as described by Tessier et al. (1979). The details of the extraction procedure are outlined in Appendix 1. The chemical extracts were analyzed for total zinc by atomic absorption spectroscopy. Two mL of each extract were sent to Chemex Labs, Vancouver, for the analysis of zinc-65 by gamma spectroscopy using a highly shielded NaI(Tl) crystal detector.

The worms from each experimental dish were extracted by sieving the sediments through a 75 µm mesh net. The worms were then separated into groups of three and each group was then placed for 24 hours in glass scintillation vials containing 5 mL of dechlorinated tap water. This procedure was followed to allow the worms to evacuate their guts and avoid the clumping that is characteristic of larger groups of worms. Clumping of the worms prevents effective evacuation of the gut and encourages coprofagy. Failure to remove gut contents can result in substantial errors in measuring tissue concentration of heavy metals (Chapman, 1985; Bindra and Hall, 1977; Chapman et al., 1980; Elwood et al., 1976). Microscopic examination of the worms indicated that gut evacuation was complete.

The worms were then pooled into groups of 30 (three samples per dish) and dried at 50°C on preweighed, acid-washed plastic strips (2 cm²). Each sample, consisting of 7 to 10 mg dry weight of worm material and the plastic strip, were digested in 2 mL of concentrated nitric acid at 90°C for four hours and then made up to 4 mL in volume with distilled, deionized water. Samples were analyzed both for total zinc and zinc-65. Blank analyses of the plastic strips were run during each digestion and indicated that they contributed only negligible amounts of zinc to each extract.

In order to determine the quantity of zinc-65 accumulated by the worms in the absence of sediments (presumably by external absorption), five samples of 30 Limnodrilus and five of Tubifex were exposed to 1 uCi of zinc-65 in 100 mL of dechlorinated tap water without sediments. During this time, no mortality was observed despite the absence of substrate and food. At the end of the week, the animals were removed, washed and placed in unlabelled dechlorinated water for 24 hours. The animals were then digested and analyzed as described above. Samples of the labelled water used in this experiment were also analyzed for zinc and zinc-65.

2.2 Bioavailability of Zinc with Sediment Depth

To evaluate the chemical partitioning and bioavailability of sedimentary zinc with sediment depth, two undisturbed cores from Station 1 in Toronto Harbour were sectioned under nitrogen at 1 cm intervals to a depth of 10 to 13 cm. Aliquots of sediment from each section were extracted for zinc by using the modified version of the sequential extraction procedure of Tessier et al. (1979). In addition to the modifications of this procedure mentioned in Section 2.1, the first four extractions (interstitial, easily-exchangeable, carbonate-bound and Fe/Mn oxide-bound) were performed under nitrogen in sealable polycarbonate tubes. All reagents were stripped of oxygen by bubbling with nitrogen gas. A nitrogen atmosphere was maintained both in the sectioning of the cores and in their extractions to prevent the introduction of oxygen into the sediments. Changes in redox conditions are known to change the chemical partitioning of zinc in the sediments (Gambrell et al., 1980; P. Campbell, pers. comm.).

2.3 Determination of the Relative Exchange Potential of Zinc Between Sediment Fractions

The movement of zinc-65 through the chemical fractions of zinc in Toronto Harbour sediments was followed over the period of a month to determine relative rates of exchange of zinc between chemical fractions and the fate of small quantities of zinc added to the sediments. Surface sediments were kept stored and oxygenated for a month before the experiment. Two samples of sediment (150 ml) were then exposed to 2 microcuries each of zinc-65. Starting immediately after dosing and over a period of one month, 11 subsamples from each sediment sample were taken over logarithmically increasing periods of time and extracted as described above to determine the chemical partitioning of both stable zinc and zinc-65. Both the activity and specific activity of zinc-65 in each chemical fraction were examined over the one month period.

2.4 Autoradiography of Lead-210 in Tubificid Worms

The mechanism of heavy metal uptake by deposit feeding tubificids was studied by incubating mixed cultures of Tubifex and Limnodrilus in sediments labelled with lead-210 and then subjecting sections of the worms to autoradiography. In this way the location of the metal accumulated in the tissues of the worms could be determined. As with the experiments using zinc-65, control worms were also incubated in water labelled with lead-210 without sediments. Separate incubations of worms were run with lead-210 rather than using the labelled worms from the previous experiments because the zinc-65 in these experiments was not amenable to autoradiography.

Sediments and worms were collected from the mouth of Keating Channel as described above. Approximately 150 ml of sediments were added to two crystallizing dishes. Since these sediments already contained large populations of tubificids, the sediments were heated at 40°C for 2 hours to kill the original fauna. Lead-210 was added (0.93×10^{-2} ucuries/ml) to the sediments a week before 100 tubificids were added to each dish. The worms were allowed to feed in the labelled sediments for 5 weeks at 9°C, after which they were sieved, washed, separated into groups of three, and placed for 30 hours in dechlorinated tap water to purge their guts. The control worms were allowed to purge their guts for 48 hours before being placed in dechlorinated water labelled with lead-210 (1.3×10^{-4} ucuries/ml). Since we found that worms incubated in water without sediments accumulated three orders of magnitude more zinc-65 than worms incubated in sediments

TABLE 2: SAMPLING SCHEME FOR ZINC-65 EXCHANGE EXPERIMENT

Sample	Time Elapsed
1	3 min
2	9 min
3	30 min
4	1.2 hr
5	3.6 hr
6	10.8 hr
7	1.4 d
8	4 d
9	12 d
10	24 d
11	33 d

of the same activity, we decreased the lead-210 activity in the control dishes by two orders of magnitude over that in the sediments in order to avoid over-exposure of the autoradiographic emulsions. After an incubation of one week, the control worms were removed and treated exactly as the worms exposed to labelled sediments.

Worms from both treatments were fixed in formalin, embedded in paraffin and sliced by microtome into 5 μ sections. The paraffin sections were mounted on glass slides, deparaffinized and dipped in NTB2 nuclear track (Kodak) emulsion at 40°C. Groups of 5 slides were then kept in the dark at 4°C for periods of 3 days, 2 weeks, and 3 weeks before development. The slides were developed in D-19 developer and fixer, then stained with hematoxylin and eosin. The slides were examined under the microscope and photographed. For a complete description of the autoradiographic procedure see Bird et al. (1986).

3.0 RESULTS AND DISCUSSION

3.1 Identification of the Bioavailable Fraction of Sedimentary Zinc to Tubificids

3.1.1 Zinc Content of Tubificid Worms

The zinc contents of both Limnodrilus and Tubifex were found to be relatively high, even after their one month exposure to sediments of low zinc content from Bowmanville Harbour. (Table 3 and Appendix 2). The mean zinc content of worms in the control experiment (224 ug/g), representing worms exposed only to labelled, dechlorinated water, was not significantly different from the zinc content of worms exposed for one and two months to Toronto Harbour sediments (256 and 259 ug/g respectively). These values are three to four times higher than zinc concentrations in tubificids measured in other studies, reviewed by Chapman et al. (1980), but fall into the range of zinc levels in samples of biota (mostly tubificids) taken by the Ministry of the Environment in Toronto Harbour (Deo Persaud, pers. comm.) and those found for tubificids from Port Hope Harbour (Hart et al., 1986).

A large difference was also evident between the two worm species, Tubifex tubifex and Limnodrilus hoffmeisteri. The zinc content of T. tubifex was almost 100 ug/g greater than Limnodrilus in both the control and experimental dishes. This difference between the two species was statistically significant (p less than 0.001) and, to our knowledge, has never been reported in the literature. The ecological significance of this difference is open to speculation on the relative tolerances of the two species to heavy metals.

3.1.2 Zn-65 Uptake by Tubificids

During the one-month exposure to Toronto Harbour sediments labelled with zinc-65, significant accumulation of zinc-65 was observed in all the worm samples for a mean accumulation of 358 Bq/g dry weight of worm (Table 3). T. tubifex accumulated about 90 Bq/g more zinc-65 activity than L. hoffmeisteri. Because of the higher zinc content in Tubifex, however, the specific activities of the zinc-65 in Tubifex and Limnodrilus were very similar at 1.32 ± 0.45 and 1.56 ± 0.4 Bq/ug zinc, respectively. The overall specific activity for both species was 1.42 Bq/ug zinc.

TABLE 3: MEAN CONCENTRATION OF ZINC, ZINC-65 AND THE SPECIFIC ACTIVITY OF ZINC-65 IN TUBIFICIDS EXPOSED TO WATER (CONTROL) AND SEDIMENTS LABELLED WITH ZINC-65

No. of Samples	Species	Mean Zinc Content ¹ (ug/g)	Mean Zinc-65 Content ¹ (Bq/g)	Specific Activity ¹ (Bq/ug zinc)
Control (-Sediment)				
5	<u>Limnodrilus</u>	186±24	$(5.12 \pm 1.27) \times 10^5$	$(2.76 \pm 0.57) \times 10^3$
5	<u>Tubifex</u>	262±35	$(2.22 \pm 0.48) \times 10^5$	$(0.87 \pm 0.25) \times 10^3$
Overall Mean		224±49	$(3.67 \pm 1.77) \times 10^5$	$(1.81 \pm 1.08) \times 10^3$
One-Month Sediment Exposure				
12	<u>Limnodrilus</u>	194±22	303±87	1.56±0.40
18	<u>Tubifex</u>	297±35	395±144	1.32±0.45
Overall Mean		256±59	358±131	1.42±0.44
Two-Month Sediment Exposure				
9/2	<u>Limnodrilus/Tubifex</u>	259±68	329±190	1.33±0.62

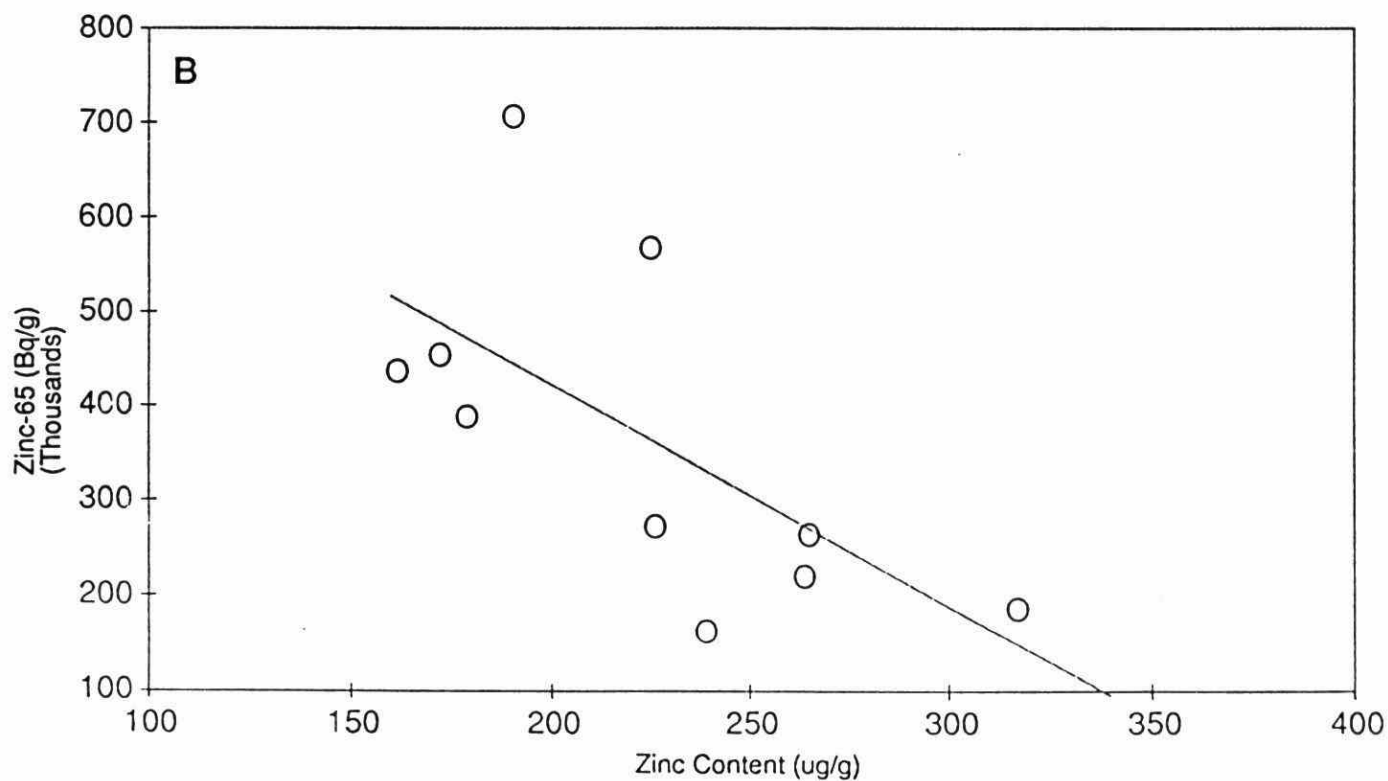
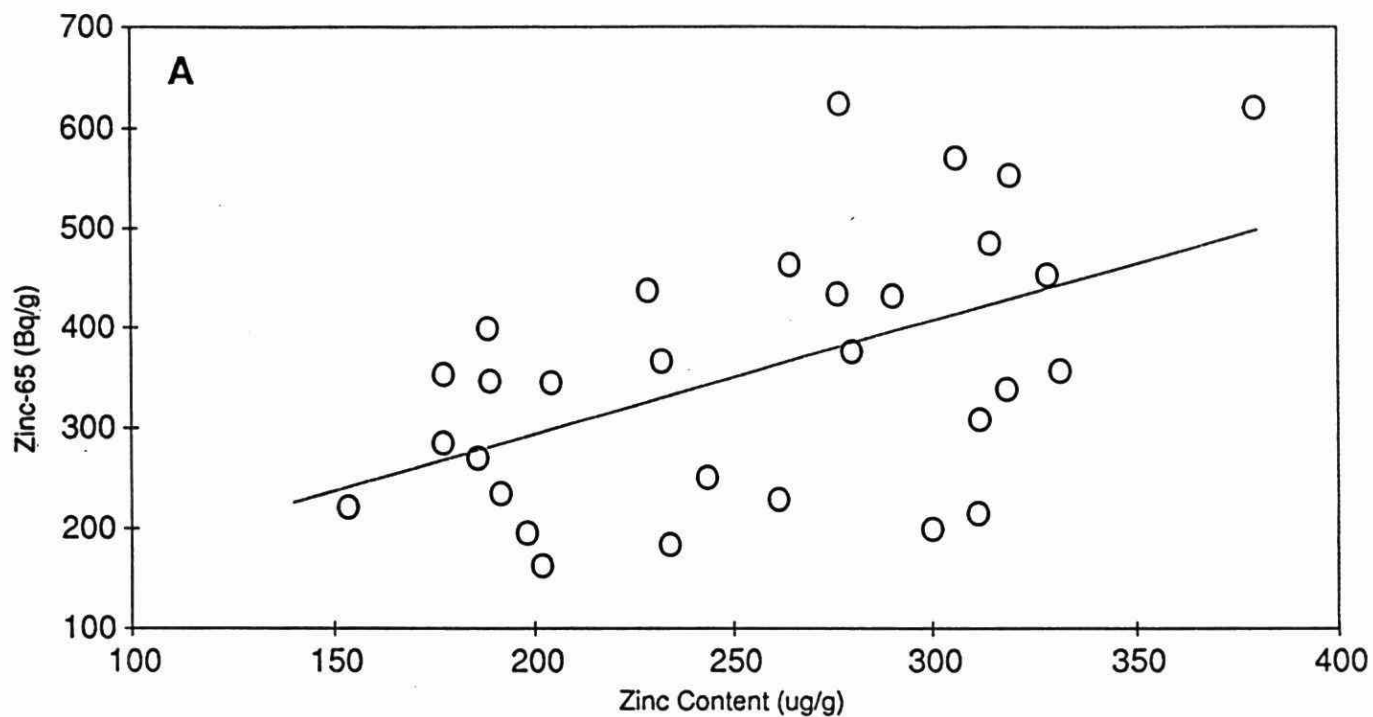
¹ Values expressed as mean ± 1 standard deviation.

Because many of the large worms died during the two-month exposure, only six out of the ten experimental dishes had sufficient mass of worms on which to make significant measurements of total zinc and zinc-65 activity. For those remaining samples, similar results were found as in the one-month exposure, although inter-specific comparisons are more difficult. The mean accumulation of zinc-65 activity during the two-month exposures (329 Bq/g) and the mean specific activity (1.33 Bq/ug Zn) were very close to those obtained in the one-month exposure. The results suggest that one month is sufficient time for equilibrium of the radioisotope between pools within the organism and the sediment.

The control experiment, where the worms were exposed only to zinc-65 without sediments, gave very different results. Although the overall activity of zinc-65 was the same in both experimental and control dishes (approximately 293 Bq/mL), the control worms accumulated three orders of magnitude more zinc-65 than the experimental worms (Table 3). Zinc activity in the worm samples in the controls ranged from 163,000 to 707,000 Bq/g of worm. Specific activities were also three orders of magnitude greater for a mean of 1.8×10^3 Bq/ug zinc. Examination of the data reveals that the mechanism of zinc-65 uptake may be very different between the experimental and control dishes. A plot of zinc-65 activity vs. the zinc content in the experimental worms (Figure 2A) produces a significant positive correlation (P less than 0.05) where the slope is equivalent to a mean specific activity of the accumulated zinc-65. These results are consistent with a bioaccumulation model in which the specific activity of the worms approaches that of a bioavailable chemical fraction(s) in the sediments. A similar plot for the control samples (Figure 2B) reveals a significant negative correlation (P less than 0.05), a finding that suggests a different mechanism of uptake.

It is possible that the worms exposed only to labelled dechlorinated water accumulated much of their zinc-65 by a process of adsorption to (or absorption through) the epidermal layer of cells on the external surface of the organism rather than through the gut. To test this hypothesis, the uptake of zinc-65 (Bq/g) in Limnodrilus and Tubifex was plotted versus the weight of the worms in each sample. Since each sample consisted of ten worms, the mass of the sample itself is proportional to the mass of an average worm in each sample. Because the surface area to volume ratio in the worms decreases with size, an inverse relationship would be expected for this mechanism of uptake (Elwood et al. 1976).

FIGURE 2:
ACTIVITY OF ZINC-65 VERSUS THE ZINC CONTENT OF TUBIFICID
WORMS EXPOSED TO LABELLED SEDIMENTS (A) AND LABELLED
DECHLORINATED WATER WITHOUT SEDIMENTS (B).



Although an inverse relationship is suggested for Limnodrilus (Figure 3), no such relationship was evident with Tubifex and neither relationship was statistically significant (P less than 0.05). In an attempt to explain these results and to determine the mechanism of heavy metal uptake by these organisms, the uptake of lead-210 by Tubifex and Limnodrilus under similar experimental conditions was studied by autoradiography. The results of this study are presented in Section 3.3.

3.1.3 Zinc and Zinc-65 in the Sediment Fractions

The results of the sequential extraction of sediments from both the one- and two-month exposures are presented in Appendix 2 to 6, and are summarized in Tables 4 and 5. Since little difference was evident between dishes or between the two subsamples within each dish, mean values only are reported in Tables 4 and 5.

The sediment extracts from both the one- and two-month tubificid exposures reveal a partitioning of zinc similar to that in fresh sediment cores (Section 3.2). Less than 1% of the sediment-bound zinc is found in the easily exchangeable fraction, while approximately 80% is found in the Fe-Mn oxide-bound and carbonate bound fractions. Only minor quantities of zinc were found in the organic (6%) and residual (9 to 13%) fractions. The two experiments differed slightly in zinc partitioning. Sediments from the two-month exposure had a slightly higher percentage of carbonate-bound and residual zinc and a lower percentage of Fe-Mn bound zinc. These differences could be due either to sediment heterogeneity or diagenetic changes occurring during the additional month.

The six chemical fractions in both experiments accumulated very different quantities of zinc-65 (Table 5). The carbonate-bound fraction picked up the largest amount of zinc-65 with an activity of 481 Bq/g in both experiments, while the easily exchangeable accumulated the smallest amount of zinc-65 at less than 20 Bq/g. The distribution of zinc-65 between fractions was disproportional to the amount of zinc in each fraction. The Fe-Mn bound fraction, for example, contained more than twice the amount of zinc than the carbonate-bound fraction, yet less than half the amount of zinc-65 activity.

FIGURE 3:
ACTIVITY OF ZINC-65 IN LIMNODRILUS EXPOSED TO LABELLED
DECHLORINATED WATER VERSUS THE AVERAGE WEIGHT
OF THE WORMS.

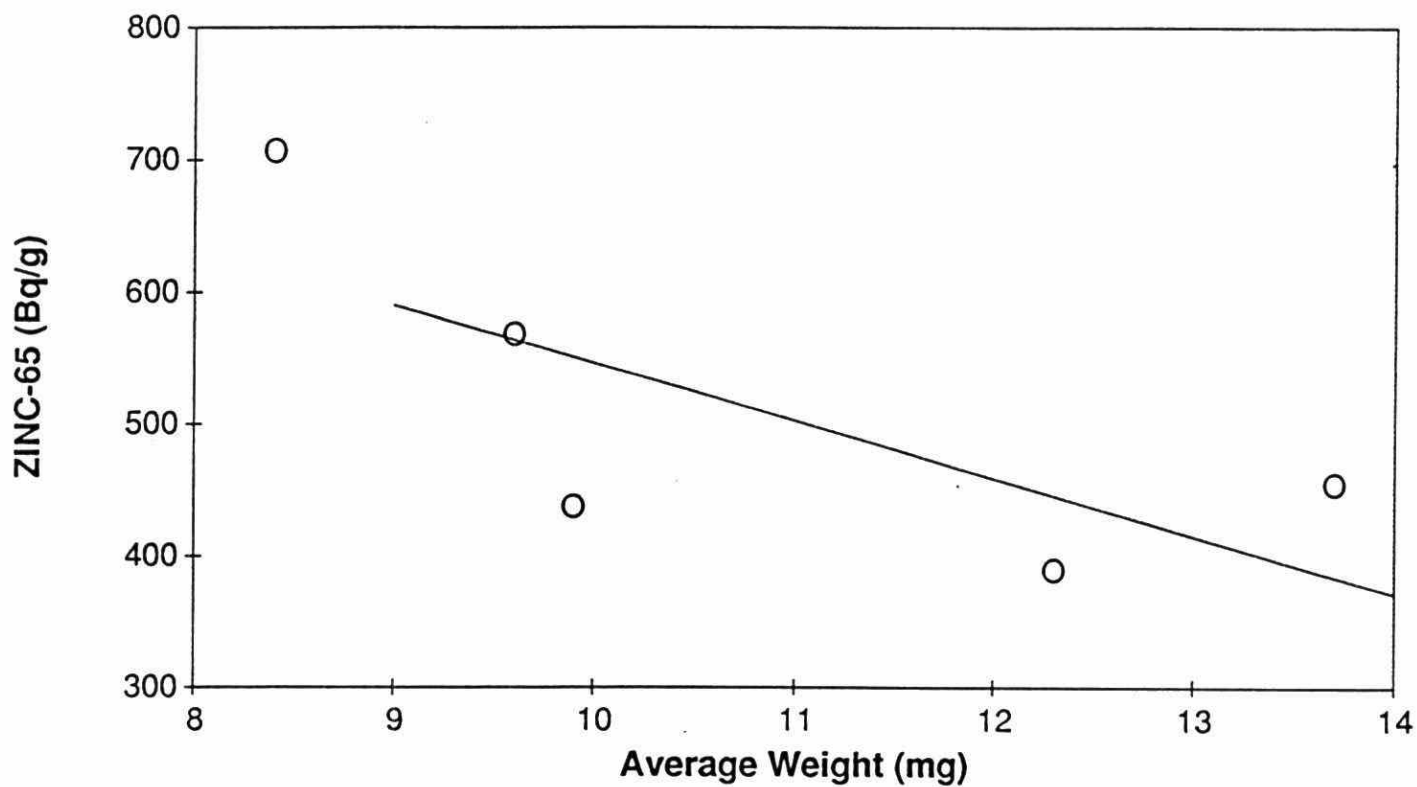


TABLE 4: CHEMICAL FRACTIONATION OF ZINC IN SEDIMENTS USED IN TUBIFICID EXPOSURES

Fraction	1	2	3	4	5	6*	7
One-Month Exposure							
Zinc (ug/g)	0.2	100	211	22	33	0.05	393
Percent of Total**	0.1	27.4	57.5	6.0	9.0	-	-
Two-Month Exposure							
Zinc (ug/g)	1.5	152	168	28	56	0.052	392
Percent of Total**	0.4	37.6	41.4	6.9	13.7	-	-

Fraction 1 = easily-exchangeable; 2 = carbonate; 3 = Fe/Mn oxide; 4 = organic; 5 = residual; 6 = interstitial; 7 = total. Values averaged over 11 dishes of two replicates each.

* Concentration expressed in mg/L.

** Percent expressed as the sum of the fractions.

TABLE 5: MEAN ACTIVITY (Bq/g) AND MEAN SPECIFIC ACTIVITY (Bq/ug zinc) OF ZINC-65 IN CHEMICAL FRACTIONS OF SEDIMENTS USED IN TUBIFICID EXPOSURES (Fraction 1 = easily-exchangeable; 2 = carbonate-bound; 3 = Fe/Mn oxide; 4 = organic; 5 = residual; 6 = interstitial)

Fraction	1	2	3	4	5	6 ¹
One-Month Exposure						
Activity	2.47±0.75	481±55	218±60	11.5±7.7	5.33±4.66	0.38±0.47
Specific Activity	12.6±7.8	4.96±0.9	1.02±0.16	0.446±0.291	0.158±0.142	4.6±1.7
Two-Month Exposure						
Activity	11.6 ± 2.8	481±96	179±48	23.8±9.5 (17.3±11.0) ²	32.8±14. (17.4±15.5) ²	1.6±0.87
Specific Activity	10.1±3.2	3.16±0.52	1.07±0.29	0.87±0.32 (0.64±0.39) ²	0.57±0.25 (0.32±0.27) ²	26.4±21.3

¹ Activity expressed as Bq/mL.

² Calculated by including values below detection limit.

The degree of labelling in each fraction is expressed by the specific activity which decreased in the following order:

- o easily exchangeable/interstitial water,
- o carbonate-bound,
- o Fe-Mn oxide-bound,
- o organically-bound, and
- o residual.

The magnitude of the specific activity seems to represent the ease of exchange of each fraction with free zinc or zinc from other fractions (see Section 3.4 and Andrews et al., 1985). In these calculations, only those samples having statistically significant numbers of counts are included (see Appendix Tables 2 to 6). This process tends to bias high some calculations of mean activities. Many of the residual extracts accumulated zinc-65 at levels less than the detection limit.

3.1.4 Comparison of Specific Activities of Zinc-65 in the Sediment Fractions and the Tubificids

Comparison of zinc-65 activity in the animals (Table 3) with zinc-65 activity in the sediment fractions (Table 5) shows that the Fe/Mn oxide fraction is closest in specific activity to that of the tubificid worms. The mean specific activity of the worms was 1.42 and 1.33 Bq/ug zinc respectively for the two exposures compared with 1.02 and 1.07 Bq/ug zinc for the specific activities of the Fe/Mn oxide-bound fraction of the sediments.

The similarity in specific activity of zinc-65 in the tubificids with that in the Fe/Mn oxide-bound fraction suggests that this metal fraction serves as a source of zinc to the worms. In the one-month experiment the Fe/Mn oxide bound fraction is the only chemical fraction in which the mean specific activity of the zinc-65 (± 1 S.D.) overlaps that of the tubificids (± 1 S.D.). In the two-month exposure, the specific activity of the zinc-65 in the Fe/Mn fraction is also closest to that of the tubificids, but the mean specific activity of the organically-bound fraction also falls within one standard deviation of the mean specific activity of the worms. This fraction, therefore, cannot be technically ruled out as a potential source of zinc.

However, because eight of the 20 samples in this fraction were below detection in counting zinc-65 activity, our estimate of specific activity based only on those samples greater than the detection limit is probably biased high. If we calculate a less biased estimate of the specific activity of the organic fraction by including those eight samples as values at the detection limit, we obtain a mean specific activity of 0.64 Bq/ug for this fraction, considerably lower than that of the zinc-65 in the worms. Similarly, the residual fraction drops from 0.57 to 0.32 Bq/ug when values below the detection limit are included.

This isotopic method of determining bioavailable fractions in sediments involves several assumptions requiring discussion. One such assumption is that sediment ingestion represents the dominant mode of heavy metal uptake by benthic deposit-feeders. This assumption will be discussed in Section 3.3 in which the results of our autoradiography experiments are presented. Another assumption is that of isotopic equilibrium between the bioavailable fraction(s) and the organism. The actual length of time required for isotopic equilibrium between the sediments and these tubificid worms is uncertain. The literature, based largely on polychaetes and deposit-feeding clams, presents a wide range of time required for equilibrium and, to complicate matters, suggests that different pools exist in deposit feeders having different turnover rates of heavy metals (Renfro and Benayoun, 1976, Renfro *et al.*, 1975). Renfro (1973) exposed the marine polychaete Hermione to zinc-65 labelled sediment and found that 60 days or more were required for this worm to approach steady-state with zinc-65 in the sediments. Luoma and Jenne (1976), however, found that after eight days cadmium-109 uptake by the deposit-feeding clam Macoma balthica was solely the result of uptake from the solute pool of cadmium-109. In this study, we attempted to be conservative and assumed equilibrium between isotopic pools required at least 30 days and possibly 60 days. The data indicate that a 30-day exposure would have been sufficient. The oligochaetes did not increase in either zinc-65 activity or specific activity between the two exposures. The mean activities of the worms in the 30 and 60-day exposures are, in fact, very close at 256 and 259 Bq/g worm respectively (Table 3).

3.1.5 The Fe/Mn Oxide Fraction as a Source of Zinc to Tubificids

The similarity in specific activity of zinc-65 in the tubificids with that in the Fe/Mn oxide-bound fraction of zinc in the sediments suggests that this metal fraction serves as a source of zinc to the worms.

The involvement of iron and Fe/Mn oxide-bound metals has been implicated in numerous studies on the bioavailability of trace metals in sediments to deposit-feeders (Luoma and Jenne, 1976a, Luoma and Bryan 1978, 1979; Tessier et al., 1984). Luoma and Bryan (1978) found that lead uptake by Scrobicularia was controlled by total lead concentration divided by iron concentrations in an acid extract of the sediments. Luoma and Jenne (1976a) demonstrated that Macoma accumulated cadmium-109 from labelled sediments composed of hydrous iron oxide particles, as long as no organic coating was present. Tessier et al., (1984) related the copper concentration in Elliptio, a freshwater mollusc, directly to copper bound to Fe/Mn oxide divided by the Fe concentration in this fraction.

These studies suggest that the iron-oxide fraction of the sediments serves directly as a source of heavy metals to benthic deposit-feeders or that iron competes with organisms for available metals. By using a very different technique, this study confirms the involvement of iron and Fe/Mn oxides in the bioavailability of heavy metals to benthic deposit-feeders. Unlike some of the studies above, however, this study points to the Fe/Mn oxide fraction as a direct source of zinc to the organisms rather than a competitor with the organisms for available zinc.

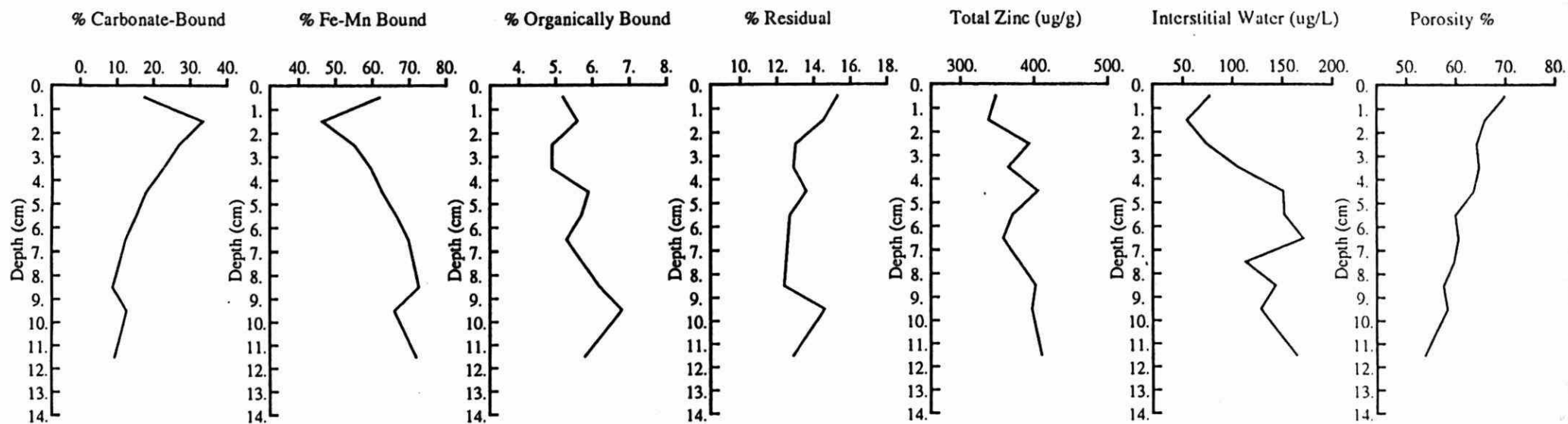
3.2 Bioavailability of Sediment-bound Zinc with Sediment Depth

3.2.1 Chemical Fractionation of Zinc with Sediment Depth

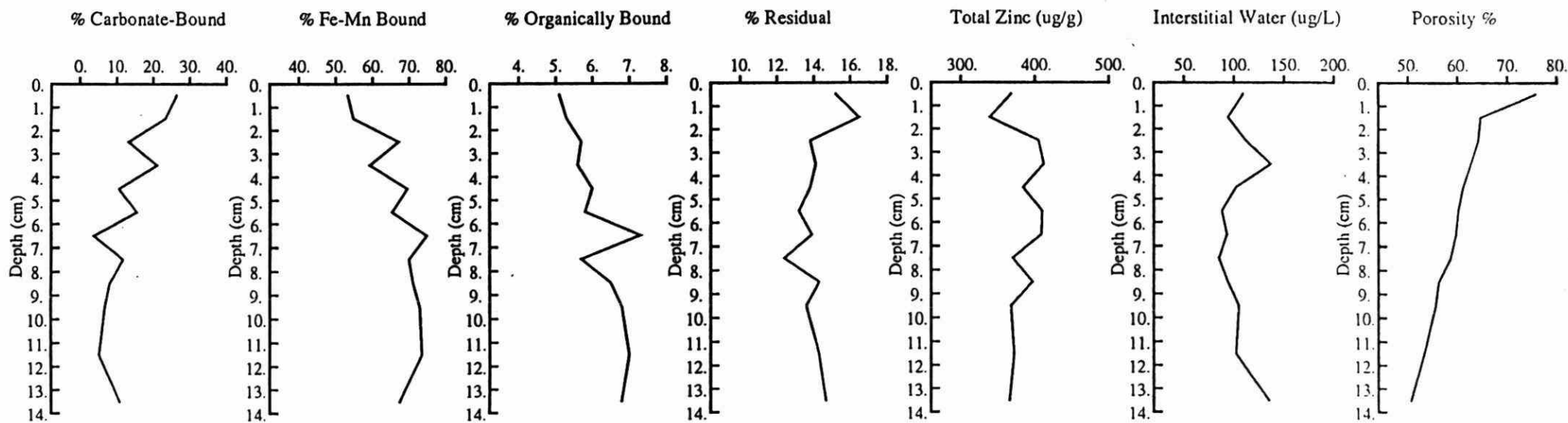
The chemical fractionation of zinc with depth in two cores from Toronto Harbour is presented in Appendix 7 and Figure 4. In both cores, porosity decreased from about 75% water to 50% water over 14 cm of depth. The smoother porosity profile in Core No. 1 suggests that this core is the less disturbed of the two, although both cores have probably been greatly influenced by harbour activities. Pore water concentrations of zinc range from 54 to 164 ug/L and appear to increase with depth in Core No. 1. This increase in depth is not apparent in the second core. The contribution of pore water to the overall concentration of zinc is very small. If we assume a sediment porosity of 75%, the interstitial and total zinc concentrations to be 150 ug/L and 400 ug/g respectively, the interstitial water only accounts for about 0.1% of the total sedimentary zinc. Almost all of the zinc, therefore, is bound to the particles.

FIGURE 4: The Chemical Fractionation of Zinc in Two Cores From Toronto Harbour

Core 1



Core 2



Total zinc in the cores, ranging from 350 to 450 ug/g, is high relative to background levels in nearshore zones of Lake Ontario (100 ug/g), but is well within range of zinc contents in river mouths and harbours (17 to 2,010 ug/g; Mudroch et al., 1986) and polluted river sediments in Europe (153 to 3,072 ug/g; Calmano and Forstner, 1983). The values in this study are comparable to those obtained in Toronto Harbour by Persaud et al., (1985). The increase of total zinc with depth in Core No. 1 was not observed in the second core or in the literature. Total zinc actually decreased with depth in two Norwegian lakes (Reuther et al., 1981) and in Lake Constance, Germany (Forstner, 1982; Forstner and Wittmann, 1983).

Exchangeable zinc in the Toronto Harbour cores was very low, below detection. The solution of $Mg\ Cl_2$ used for these extractions actually lost contaminant levels of zinc to the sediments, which acted in this case as a cation adsorber. In subsequent sequential extractions of Toronto Harbour sediments (Sections 3.1 and 3.3), an ultrapure grade of the salt was used, and measurable levels of easily-exchangeable zinc were obtained. Nevertheless, easily-exchangeable zinc was always less than 1.6% and frequently less than 0.2% of the total zinc content. Reuther et al. (1983) also found very low percentages of cation exchangeable zinc (1 to 6%) in cores from the two Norwegian lakes mentioned above. Similarly, low levels of exchangeable zinc were found by Calmano and Forstner (1983) in European rivers and by Rapin et al. (1983) in Mediterranean sediments (less than 3%). Tessier et al. (1979) also found levels of easily-exchangeable zinc below detection in sediments from the Yamaska and St. Francis Rivers, Quebec.

Most of the particle-bound zinc, about 80%, resides in the carbonate-bound (13 to 17%) and Fe/Mn oxide-bound fractions (63 to 67%). Similarly, high levels of zinc were found in analogous chemical fractions of sediments extracted in the studies mentioned above (Forstner, 1982; Calmano and Forstner, 1983; Rapin et al., 1983; Ruether et al., 1983). Carbonate-bound zinc in Core No. 1 increases for the first 2 cm then decreases over the length of the core. A similar subsurface maximum in this chemical fraction was observed for zinc in Lake Constance sediments (Forstner, 1982) and for cobalt in sediments from the Ottawa River (Andrews et al., 1985). This decrease in carbonate-bound metals with depth in the sediments is probably caused by a parallel decrease in pH that results in a dissolution of carbonate compounds. The subsurface maximum is less easily explained.

In the Ottawa River sediments, low levels of carbonate-bound cobalt near the sediment surface were associated with high levels of easily-exchangeable cobalt. The latter fraction may compete with the carbonate compounds for the metal. A similar trend in easily-exchangeable zinc was not evident in the cores from Toronto Harbour. Moreover, a subsurface maximum in carbonate-bound zinc did not occur in the second core.

The Fe/Mn bound zinc increased with depth in both Toronto Harbour cores. This increase from about 50 to 70% of the particle-bound zinc corresponds well with the decrease in carbonate-bound zinc. It seems that these two fractions virtually control the overall partitioning of the metal in the sediments. Slight chemical or diagenetic changes with depth result in the transfer of metal from one of the two fractions to the other, while significant transfer of zinc to other fractions does not appear to occur.

Of the remaining fractions, organically-bound zinc increases slightly with depth, from about 5 to 7%, while no trends are apparent in the 14 to 16% of the sediment-bound metal classified as residual and extracted only in hot nitric acid.

3.2.2 Implications of the Chemical Fractionation of Zinc with Depth for Benthic Deposit-Feeders

The results presented above on the fractionation of zinc with sediment depth have important implications for the ultimate accumulation of zinc by benthic oligochaetes. From Section 3.1, we know that the Fe/Mn oxide-bound fraction of zinc is the likely source of this metal to tubificid worms. Figure 4, showing the vertical distribution of this fraction with depth, indicates that between 50 and 70% of the metal is found in this chemical fraction over the upper 10 cm of sediments. This means that in general 50 to 70% of sediment-bound zinc is available to tubificids.

The exact quantity of available zinc will, of course, depend on the feeding habitats of the worms and their vertical distribution in the sediment column relative to that of the Fe/Mn oxide-bound zinc fraction. Studies by Brinkhurst *et al.* (1969), Milbrink (1973) and Krezoski *et al.* (1978) suggest that the majority of oligochaetes are found in the uppermost 6 cm of sediment. Krezoski *et al.* (1978) studied sediments from Lake Huron similar to those collected in our study having a brown flocculant layer overlying firm, grey, sandy silt.

When the brown layer was only about 1 cm, as we found in our cores, most of the oligochaetes were in the 0 to 5 cm interval. None were below 10 cm. Based on these results, we expect the majority of the worms to be exposed to bioavailable levels of zinc between 45 to 65% of the total zinc content of the sediments (We are using the less disturbed Core No. 1 for these calculations). Since tubificids normally feed at depth and deposit their feces on the sediment surface, they are likely to ingest sediments having levels of bioavailable zinc towards the higher extreme of this range.

3.3 Autoradiography of Lead-210 in Tubificid Worms

The results of the autoradiographic experiments, designed to locate the sites of uptake of Pb-210 in the tubificid worms, can be seen in Figures 5 to 9. In the autoradiographic procedure, opaque silver grains are precipitated in those tissues where lead-210 has accumulated. The silver grains can be seen as sharp, dark spots on the photographs. The photographs indicate the following:

- (1) Significant quantities of lead-210 were accumulated both in worms exposed to labelled water and to labelled sediments. In both cases, the lead-210 was found in identical locations.
- (2) Most of the metal is found in the internal tissues of the worms. Very few silver grains were found on the external surfaces. Silver grains were associated with the cuticle only on the anterior and posterior-most segments of the organisms and only in a few worm sections.
- (3) Lead-210 did not accumulate significantly in the epidermal cells, muscle cells, cells in the gut walls or in the blood vessels. A darkening of the circular musculature in the body wall was observed, but this did not appear to be caused by an accumulation of silver grains.
- (4) The majority of the lead-210 was found in three locations:
 - (1) free in the coelomic cavity,
 - (2) in lens-shaped pits in the walls of blood vessels, and
 - (3) in the nephridial funnel, around nephridial canals and associated nephridial tissues.

The granules were most abundant in the third location; that is, associated with the nephridia.



Figure 5: **AUTOGRAPH OF A LONGITUDINAL SECTION OF A TUBIFICID WORM EXPOSED TO LEAD-210 IN DECHLORINATED WATER:** Posterior segment of worm showing lead-210 on external surface (arrows) and between muscle fibres (circles). Note that the lead-210 was not taken up substantially by the muscle fibres or the epidermal cells.

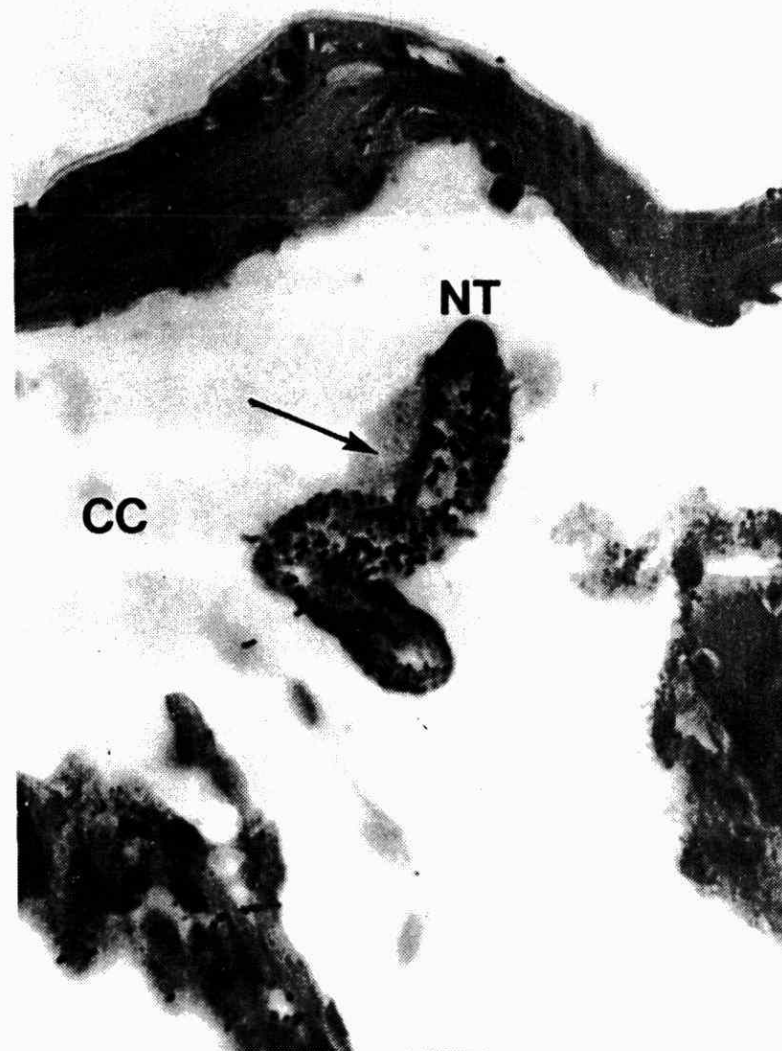


Figure 6: **AUTORADIOGRAPH OF A LONGITUDINAL SECTION OF A TUBIFICID WORM EXPOSED TO LEAD-210 IN DECHLORINATED WATER:** Segment of worm showing the epidermal and muscular layers of the body wall, a cross-section of the gut (lower left) and nephridial tissue (NT) in the coelomic cavity (CC) in which a large quantity of lead-210 has accumulated.

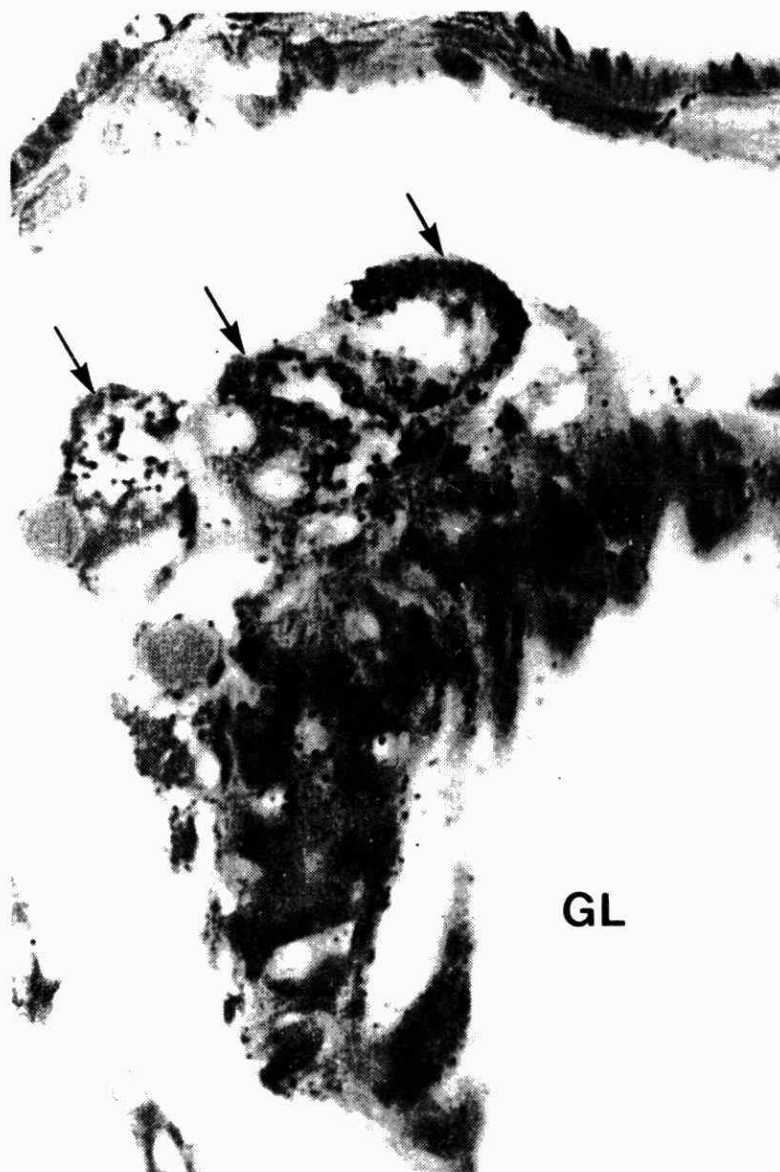


Figure 7: **AUTORADIOGRAPH OF A LONGITUDINAL SECTION OF A TUBIFICID WORM EXPOSED TO LEAD-210 IN DECHLORINATED WATER:** Segment of worm showing accumulation of lead-210 in the nephridial tissue associated with a vascular network on the ventral side of the gut wall (arrows). The lumen of the gut can be seen on the lower right (GL).

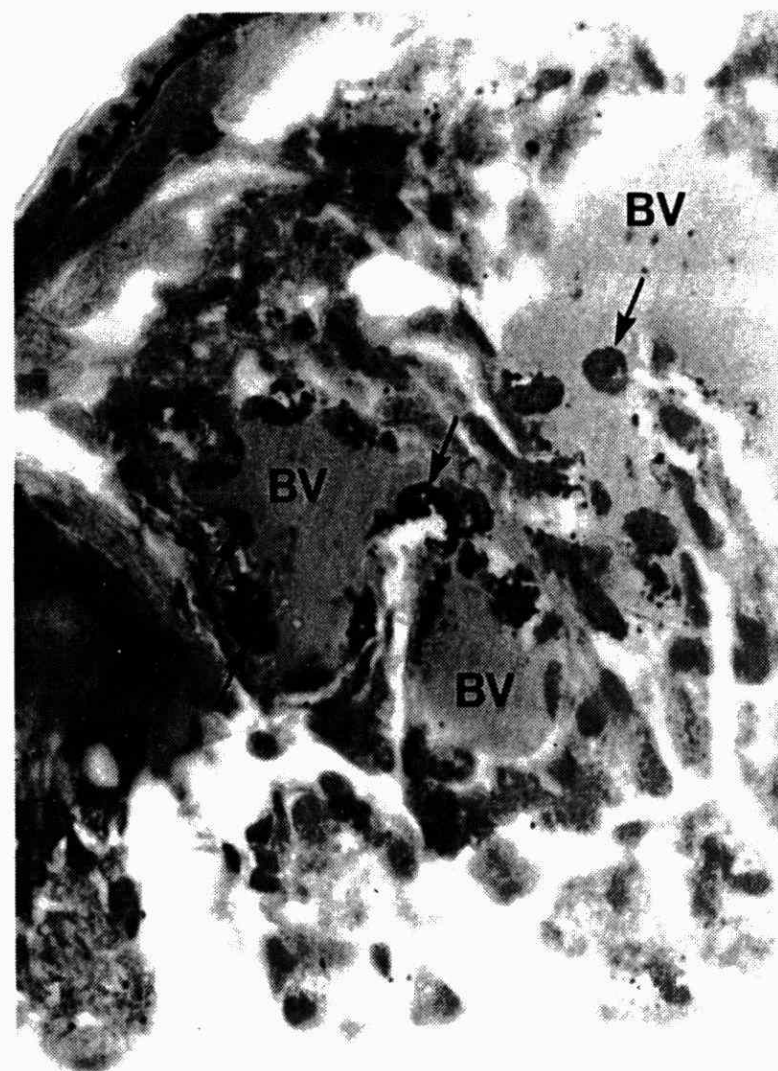


Figure 8: **AUTOGRADIOGRAPH OF A LONGITUDINAL SECTION OF A TUBIFICID WORM EXPOSED TO SEDIMENTS LABELLED WITH LEAD-210.** The lead-210 (arrows) was accumulated in pits in the walls of the blood vessels. The blood vessels are the large clear bodies in the centre of the photograph (B.V). Note that the blood itself, consisting of a pigmented plasma, did not accumulate lead-210.



Figure 9: AUTORADIOGRAPH OF A LONGITUDINAL SECTION OF A TUBIFICID WORM EXPOSED TO SEDIMENTS LABELLED WITH LEAD-210. Posterior segment of worm showing accumulation of lead-210 in the spaces between muscle fibres (arrow). This figure is similar to Figure 5 in which the worms were exposed only to labelled water. The posterior and anterior-most segments appear to be active sites of lead uptake both with and without sediments.

- (5) Despite the fact that worms in the sediments were exposed to activities of lead-210 almost two orders of magnitude greater than those in water alone, there was no obvious difference between the two groups in the amount of lead-210 accumulated.
- (6) Local accumulations of lead-210 occurred in spaces between muscle bundles at the anterior and posterior segments of worms under both experimental conditions.

3.3.1 Mechanism of Uptake of Heavy Metals by Tubificids

The results of these experiments, in which tubificids were exposed to lead-210 (and zinc-65) in water, indicate that tubificids can accumulate large quantities of heavy metals directly from solution. Accumulation of soluble heavy metals occurs through the epidermis and/or through the gut wall. Since few silver grains were evident in the epidermal cells themselves or in cells of the gut wall, it is impossible to determine conclusively which is the main site of heavy metal uptake. However, the local accumulations of silver grains both externally and internally in the anterior and posterior segments on some of the worm sections suggest that in these segments active uptake of soluble lead occurs across the epidermis. This conclusion is consistent with Figure 3 which also implicates the epidermis as a site of uptake of zinc-65. Regardless of the site of uptake, the absence of lead-210 in either the epidermal or the intestinal cells suggests that accumulation of the metal in specific internal tissues of the worms is both rapid and efficient. Concentration of much of the lead-210 in the nephridial tissue suggests that an efficient mechanism exists for excreting the lead.

While it is evident from these results that tubificids can absorb metals dissolved in solution, the mechanism of uptake in sediments when metals are particle-bound remains uncertain. There is even a question as to whether particle-bound metals serve as a source of metals to deposit-feeders. Obviously, even particle-bound metals must be solubilized at some point before absorption is possible. Most authors assume an ingestive mechanism of metal uptake by which sediment-bound metals are ingested, solubilized in the gut (or intracellularly) and absorbed through the gut wall. Such a mechanism is implicit in the use of sediment fractions to predict heavy metal burdens in benthic organisms. Bryan and Hummerstone (1978) and Bryan and Ussal (1978) found that large proportions of most metals were concentrated in the digestive glands of deposit-feeding

bivalves. From this they concluded that metals are chiefly absorbed from ingested sediments. The ingestive mechanism is also supported by Marquenie (1983) who exposed containers of Macoma and sediments contaminated to different extents to the same natural water. Concentrations of metals in the organism reflected metal concentrations in the sediments rather than the water above.

Not all studies support the ingestive mechanism of metal uptake. Such dissenting studies imply that only soluble, interstitial metals are available to the organisms. The accumulation of heavy metals in the digestive glands of deposit-feeding bivalves by Bryan and Hummerstone (1978) and Bryan and Usyal (1978) does not provide conclusive evidence for the ingestive uptake of sediment-bound metals. As we found in the autoradiographic experiments, lead-210 was accumulated in the same tissues of the worm exposed to the isotope both in water and sediments. Dean (1974) found that tubificids accumulated zinc-65 directly from water (without sediments), but not from labelled sediments. His observations contradict our study in which we found substantial uptake of zinc-65 from labelled sediments by Tubifex and Limnodrilus. Prosi (1979) suggested that interstitial cadmium rather than sediment particles formed the dominant source of this metal to Tubifex grown in Rhine River sediments. Re-examination of Prosi's data, however, may indicate just the opposite. Interstitial bioconcentration factors for Tubifex grown in Rhine River and Lake Constance sediments were very different (1.8 and 0.3, respectively) while bioconcentration factors based on the whole sediments were quite similar (7.34 and 7.71), despite very different levels of cadmium in the two sediments (5.48 and 0.35 ug/g). These calculations actually suggest that particle-bound rather than interstitial cadmium is the source of this metal to the worms. Obviously the source of metals to deposit-feeders in sediments remains somewhat unclear.

Although the mechanism of heavy-metal uptake from the sediments cannot be conclusively determined from our results, several points do emerge. First, absorption of lead-210 and zinc-65 occurs both in the presence and absence of sediments. Whatever, the source of the metal, soluble or particulate-bound, it is accumulated in the same tissues of the organism. Second, in the presence of sediments only a fraction of the metal is available to the worms. This was seen both in the zinc-65 experiments, in which the worms absorbed three orders of magnitude more zinc-65 from water without sediments, and in the lead-210 experiments where similar accumulations of lead-210 occurred under both treatments despite much lower concentrations of the isotope in the water. Obviously, soluble metals are much more available to benthic deposit-feeders

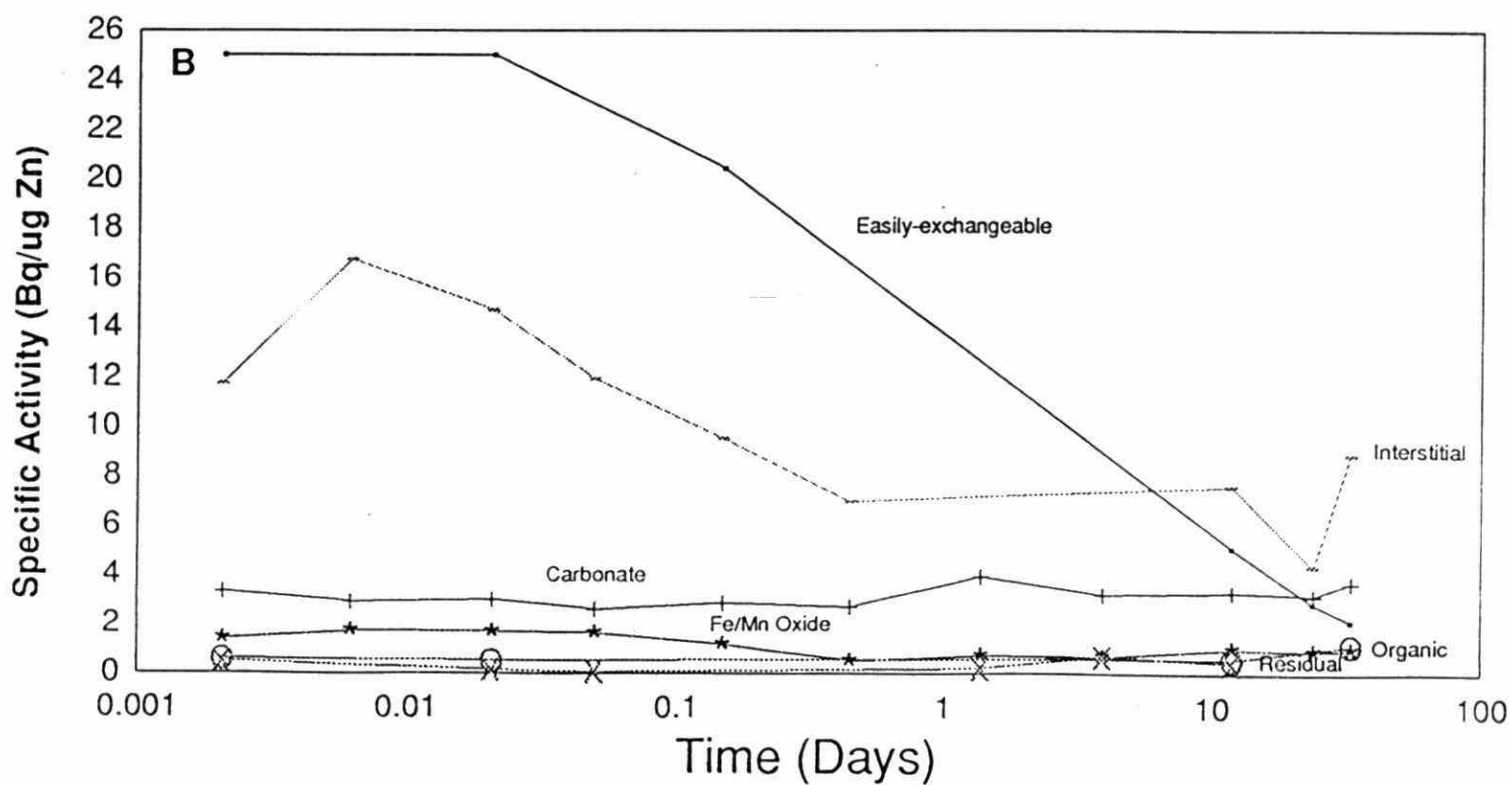
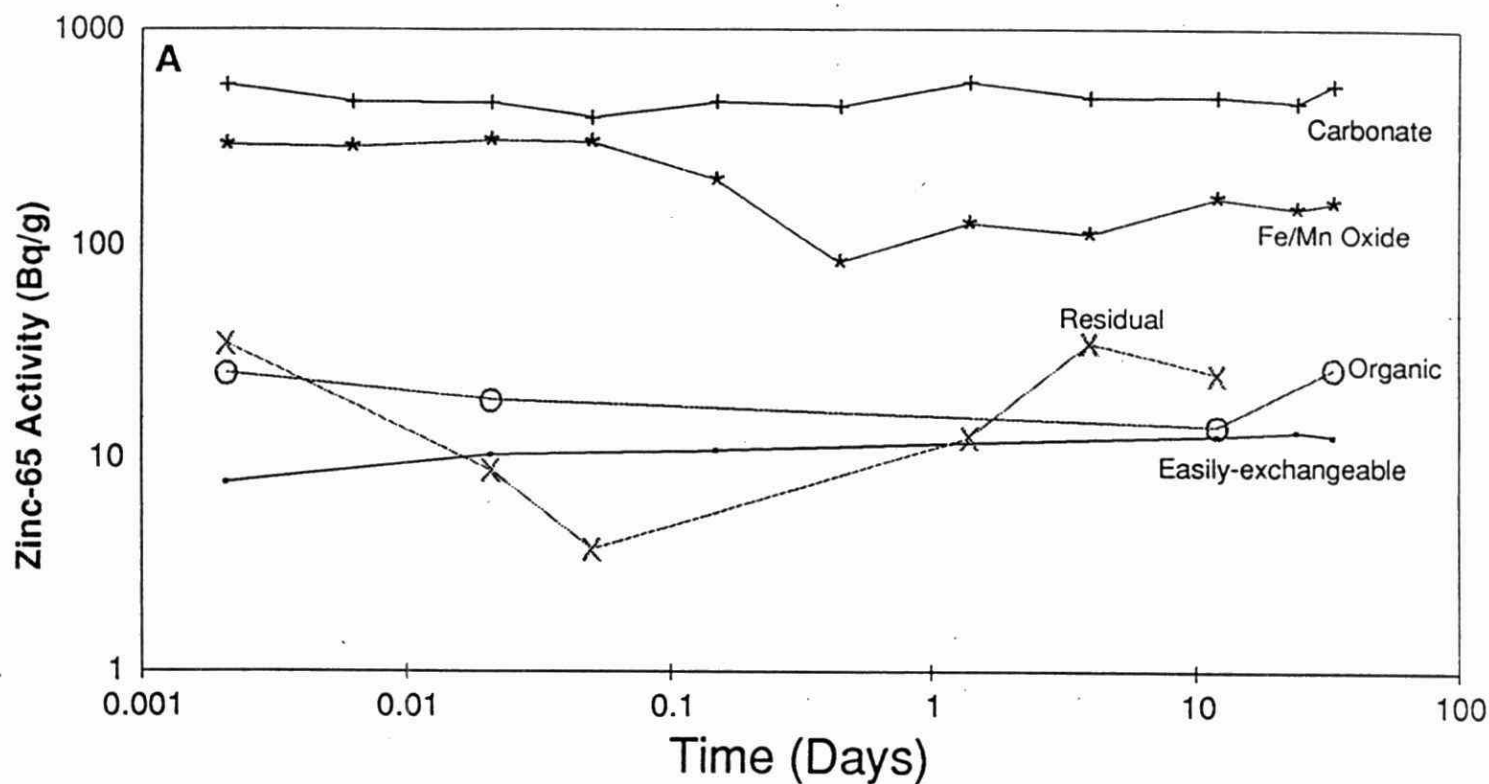
than particle-bound metals. By binding with metals, sediments decrease their bioavailability by orders of magnitude. Third, the local accumulation of lead in the posterior and anterior-most segments of worms exposed to labelled sediments (Figure 8), suggests that a certain soluble fraction of lead in the sediments is taken up by the epidermis in these segments. Finally, the results of the zinc study linking bioavailability to the Fe/Mn oxide fraction of zinc, and certainly the weight of scientific opinion support the hypothesis that certain fractions of sediment-bound metals are also available to benthic deposit-feeders.

3.4 Relative Exchange Potential of Zinc in Chemical Fractions of Toronto Harbour Sediments

When added to Toronto Harbour sediments, inorganic zinc-65 was rapidly taken up almost exclusively by the sediment particles. Within three minutes after dosing, over 99% of the zinc-65 was associated with the particulate fraction and only 0.4% with the interstitial water. This estimate is based on an assumption of 75% porosity and gross activities of 0.83 Bq/mL and 692 Bq/g for the interstitial water and particulate sediments, respectively (Appendix 8). Most of the zinc-65 goes directly into the carbonate-bound (65%) and the Fe/Mn oxide-bound (30%) fractions. Much smaller quantities are taken up by the exchangeable fraction (0.8%), residual fraction (4%) and interstitial water (less than 0.4%).

Figure 10A, showing mean activity in each fraction versus time, indicates that, over the month-long experiment, there is little net change in zinc-65 activity in each chemical fraction or exchange of the isotope between sediment fractions. Fluctuations in activity, such as those occurring in the residual and interstitial fractions, are caused primarily by the low counting rates and the resulting high statistical variability of these samples. The decrease in activity in the Fe/Mn oxide fraction at 3.6 and 10.8 hours into the experiment, however, is more puzzling. Between replicate samples 5A and 5B (Appendix 8), the zinc-65 activity in the Fe/Mn oxide fraction drops precipitously by more than one-half. There is no change, however, in the total zinc concentration in this fraction during this time. A parallel drop in specific activity is also evident (Figure 10B). We believe that this drop in zinc-65 activity in the Fe/Mn oxide fraction is an artifact caused by a drop in counting efficiency for this series of samples. The true behaviour of this fraction is probably like that of the carbonate-bound fraction where little change in activity occurs during the experiment.

FIGURE 10 :
ACTIVITY (A) AND SPECIFIC ACTIVITY (B) OF ZINC-65 IN CHEMICAL
FRACTIONS OF TORONTO HARBOUR SEDIMENTS VERSUS TIME AFTER
ADDITION OF THE LABEL.



Examination of the specific activity of zinc-65 in each fraction with time (Figure 10B), reveals that zinc-65 was not taken up in proportion to the size of each chemical fraction. Thus, the easily-exchangeable and interstitial fractions, together containing less than 2% of the total sediment-bound zinc, were the most heavily labelled fractions, with initial specific activities of 25 and 11.8 Bq/ug zinc. In comparison, the carbonate and Fe/Mn oxide-bound fractions, having over 80% of the total sedimentary zinc, took up proportionally less of the label, with mean-specific activities of only 3.33 and 1.39, respectively. The organic and residual fraction took up the least proportional amounts of zinc-65, with initial specific activities of 0.60 and 0.51 respectively.

The dramatic decrease in specific activity of the easily-exchangeable fraction is directly related to diagenetic changes during the course of the experiment. Between 4 and 12 days, easily-exchangeable zinc increased by an order of magnitude, from about 0.5 ug/g to 5.0 ug. This movement of zinc represents a shift of only 1.5% of the total zinc content of the sediments, and may be due to an increasing anoxia. Presumably, the zinc came from a fraction such as the carbonate-bound fraction, where the specific activity was lower than that in the easily-exchangeable fraction. The result of this shift was a dilution of the zinc-65 with stable zinc and a decrease in the specific activity of the easily-exchangeable fraction. A similar decrease in specific activity of the interstitial zinc fraction can also be partially attributed to a two-fold increase in interstitial zinc during the month-long experiment.

Based on these measurements of specific activity in Figure 10B, it is possible to indicate the relative ease of exchange of zinc between each chemical fraction of the sediments and a hypothetical pool of free zinc. The relative order in decreasing magnitude is as follows:

- o exchangeable zinc,
- o interstitial zinc,
- o carbonate-bound zinc,
- o Fe/Mn oxide-bound zinc,
- o residual zinc, and
- o organic zinc.

The results of this study are similar to those obtained by Andrews *et al.* (1985). Adding cobalt-60 to natural sediments, these authors also found that little net exchange of cobalt-60 occurred between sediment fractions after the initial uptake. As in this study, they found that cobalt-60 was non-proportionally distributed between the chemical fractions. Both studies indicate that uptake and exchange kinetics determine the chemical distribution of heavy metals introduced to natural sediments. When a heavy metal is added to sediments, it will partition between the various chemical fractions in a manner dependent upon the kinetics of exchange between each fraction or between each fraction and a free form of the metal, perhaps in the interstitial phase. When a radionuclide of a heavy metal is introduced, each chemical fraction of the sediments should approach the same specific activity if sufficient time is allowed, each fraction is equally accessible to the radionuclide and each exchange reaction is reversible.

Evidently, in these experiments and those of Andrews *et al.* (1985), these criteria for equilibrium were not met. Figures 10A and 10B show that the initial distribution of zinc-65 between chemical fractions, measured within minutes of addition, is retained for the duration of the experiment. This distribution, therefore, represents a meta-stable equilibrium. The time to reach true equilibrium is at least in the order of months, if not years.

3.4.1 Implications of a Meta-Stable Equilibrium to the Bioavailability of Metals in Sediments

The possibility of such a meta-stable distribution has important implications when considering the fate and bioavailability of metals recently introduced to the sediments. Because recently introduced trace metals are not necessarily distributed between sediment fractions in proportion to the size of each fraction, they may accumulate for long periods in fractions which are either highly available to deposit-feeders or not at all. Their distribution will depend entirely on the kinetics of the exchange reactions involved. For example, based on the distribution of total zinc in this experiment we would expect that almost 45% of the added zinc-65 would be retained in the most available Fe/Mn oxide fraction. Instead, only 30% of the zinc-65 was accumulated in this fraction. Recently added zinc is therefore less available to organisms than suggested by the chemical partitioning of zinc in these sediments.

Determination of the availability of a recently added metal will depend not only its absolute uptake by a bioavailable fraction, as controlled kinetically, but also on the size of the fraction. For a given uptake of trace metal, a bioavailable fraction already containing a large amount of this metal will experience a smaller proportional increase in this metal than that of another bioavailable fraction containing less of the metal. The smaller the proportional increase in a trace metal within a bioavailable fraction, the less significant the increase in exposure of the deposit feeder to the metal. It is of course possible that both the uptake kinetics and the size of the fraction are functionally related.

In this experiment measurements of the specific activity of zinc-65 in each chemical fraction combine both the absolute uptake of the label and the size of the each zinc fraction to express the fractional increase in zinc in each fraction for a given addition of zinc to the sediments. Consideration of both the specific activity of each fraction and its bioavailability, therefore, indicates the fate of small quantities of zinc added to the sediments.

In general, for any metal-radionuclide system, the greater the specific activity in a bioavailable fraction, the greater the exposure of an organism to the trace metal. In Toronto Harbour sediments, the specific activity of zinc-65 in the bioavailable Fe/Mn fraction was low relative to other fractions. Three other chemical fractions, (exchangeable, interstitial and carbonate bound) had higher specific activities and therefore, exchanged much more freely with other fractions or soluble zinc. The effects of small additions of zinc to the system are therefore mitigated both by the slow rates of uptake of zinc by the Fe/Mn oxide fraction and the magnitude of the fraction itself.

3.5 Examination of Ministry Data on Zinc in Biota and Sediments

Data from 42 stations of the Ministry's In-Place Pollutants Program (Appendix 9) were examined to determine whether zinc content of the biota could be predicted from zinc concentrations in the sediments. Since our experiments showed that the Fe/Mn oxide fraction of zinc served as the source of this metal to tubificids in Toronto Harbour sediments, it was of interest to determine whether a similar conclusion was derivable from the Ministry's data representing 12 distinct study areas.

TABLE 6: RELEVANT DATA AVAILABLE FROM IN-PLACE POLLUTANTS PROGRAM

Parameter	Description	Comments
Biota (Zn)	Non-Specific	Mostly tubificids
Interstitial Water	-	-
F1	Cation exchangeable and adsorbed zinc	Analogous to "easily-exchangeable" fraction in present study
F2	Specifically adsorbed and easily reducible zinc	Mn oxide, amorphous Fe-oxides and carbonate-bound zinc, analogous to "carbonate-bound" and part of "Fe/Mn oxide bound" fractions in present study
F3	Organic and sulphide-bound zinc	Analogous to "organically-bound" fraction in present study
F4	Moderately reducible zinc	Hydrous iron oxide bound zinc, analogous to part of "Fe/Mn oxide bound" fraction in present study
Res	Residual zinc	Analogous to "residual" fraction in present study
Total	Total sediment digest	-
Fe	Bulk iron concentration	-
% Sand	All particles greater than or equal to size designated as sand (88-62)	-

The sediment data available to this study from the In-Place Pollutants Program (Table 6) consisted of concentrations of zinc in biota, interstitial water and five chemical fractions of the sediment. Also available were bulk iron concentrations and various bulk parameters such as loss-on-ignition and particle size. The five chemical fractions were obtained by sequential extractions of those sediment particles less than 63 μm .

Following studies such as those by Tessier *et al.* (1984) and Luoma and Bryan (1982), we first examined the correlation of zinc in the biota with that in the interstitial water, the various sediment fractions (F1-F4), residual zinc, total zinc, total zinc/total iron, the partial sum of F2 and F4 and the percent sand in the bulk sediments. The partial sum of F2 and F4 was chosen to resemble the Fe/Mn oxide bound fraction in the current study. Total zinc was normalized with respect to iron content because previous studies (Luoma and Bryan, 1978; Tessier *et al.*, 1984) have suggested a role of iron in competing for metals in the gut of deposit-feeders. In addition to these individual correlations, we conducted a step-wise multiple correlation with zinc concentration in the biota as the dependent variable and zinc concentrations in the interstitial water, F1, F2, F3, F4 and the residual fractions as the independent variables. The results of the individual correlations are shown in Table 7 where values of r , the correlation coefficient, are tabulated. None of the correlations, including the partial sum $F2 + F4$, are statistically significant. The step-wise multiple regression, as well, failed to give significant relationships. Of all the variables the easily-exchangeable fraction, F1, was the most significant and the moderately reducible fraction, F4, the least significant fraction in explaining the variation in body burdens of zinc.

The failure to obtain significant correlations and corroborate the results of this study are, perhaps, not surprising. The results from the Ministry's study and ours are not truly comparable. The Ministry's data are based on sieved samples, while those from this study and most others are based on extractions of the bulk sediments. The chemical partitioning of zinc in the Ministry's samples are as a result, very different from those of this study and others (e.g., Reuther *et al.*, 1983). In the Ministry's samples, 31 to 94% of the total zinc is found in the organic fraction (F3), while in our study only 5 to 6% is organically-bound. The bulk of the zinc in our study is found in the carbonate and Fe/Mn oxide fractions.

TABLE 7: CORRELATION COEFFICIENTS (r) FOR RELATION OF ZINC IN BIOTA TO ZINC IN THE SEDIMENT FRACTIONS FOR 39 STATIONS OF THE IN-PLACE POLLUTANTS PROGRAM

	Interstitial	Sediment Fraction(s)				Res	Total	Total/Iron	F2 and F4	% Sand
		F1	F2	F3	F4					
r	0.042	0.249	0.058	-0.184	0.035	-0.120	-0.181	-0.200	0.055	0.204

Significant correlations between zinc in the Fe/Mn oxide fraction of the sediment and zinc content of the tubificid worms in our own sediment-tubificid incubations would, of course, provide the best corroboration of the results of this study and our technique. Unfortunately, all these incubations were conducted on aliquots of sediment taken from one homogenized sediment sample. Since all the sediment samples in our incubations are essentially subsamples of the same sediment sample, there was insufficient variation in the concentration of zinc in each sediment fraction to develop significant correlations. Corroboration of our technique, from field data will have to depend on future field and laboratory studies run in parallel.

4.0 CONCLUSIONS AND RECOMMENDATIONS

The following conclusions can be drawn from this study.

1. Fe/Mn oxide-bound zinc is the chemical fraction of zinc serving as the primary source of this metal to tubificid worms in Toronto Harbour sediments.
2. Most of the particle-bound zinc in Toronto Harbour sediments resides in the carbonate-bound (13 to 17%) and Fe/Mn oxide-bound (63 to 67%) fractions. Only minor amounts are found in the organically-bound (5 to 7%), easily-exchangeable (less than 2%) and residual fractions (14 to 16%).
3. Based on the vertical distribution of the Fe/Mn oxide fraction of zinc, 50 to 70% of sediment-bound zinc is available to tubificids.
4. Inorganic zinc added to the sediments is rapidly taken up by the particulates. A meta-stable equilibrium is established where each fraction accumulates a different proportion of the added zinc.
5. Based on Fe/Mn oxide-bound zinc as the bioavailable fraction, recently added zinc may be less available to organisms than suggested by chemical fractionation of aged surface sediments. The specific activity of a labelled bioavailable fraction indicates the increase in exposure of an organism to small additions of metal to the sediments.
6. Autoradiographic analysis of worm tissues from tubificids exposed to lead-210 in water and sediments indicates that soluble lead is taken up very readily, presumably through the epidermis of the organisms. Particle-bound metals are much less available than soluble forms. The metal is rapidly and efficiently accumulated in specialized cells of the worm. The mechanism of uptake of sediment-bound metals remains uncertain although some of the metal is probably taken up through the epidermal cells in the posterior and anterior segments of the worm.

Additional experiments using the sediment-metal-radionuclide system are recommended to determine the bioavailable fraction(s) of other metals in freshwater sediments. Further autoradiographic experiments are also recommended to clarify the mechanism of heavy metal uptake by tubificids in sediments.

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APPENDIX 1

Sequential Extraction Procedure For Toronto Harbour Sediments

SEQUENTIAL EXTRACTION PROCEDURE

For Toronto Harbour Sediments

Extraction of Interstitial Water

Add about 10 g of sediment to each centrifuge tube. Purge and cap under N_2 . Centrifuge the sediments. Pour off the interstitial water into plastic vials containing 0.1 mL of 0.10 N HNO_3 . Recap the vials under N_2 .

Add about 1 to 1.5 g of each sediment sample to pre-weighed centrifuge tubes. Flush and cap quickly under N_2 . Reweigh each centrifuge tube to determine the weight of the sample.

First Extraction: Exchangeable Zinc

Add 8 mL of deoxygenated $MgCl_2$ solution (1M $MgCl_2$, pH 7.0) to each tube. Purge and cap under N_2 . Shake for one hour on shaker. Centrifuge. Pour off the supernatant into vials (or suck off with pipet). Flush with N_2 . Add 8 mL of deoxygenated DDW. Purge and cap under N_2 . Shake to resuspend the pellet. Centrifuge. Pour off and discard the supernatant. Purge and cap under N_2 .

4. Second Extraction: Carbonate Bound Zinc

Add 8 mL of deoxygenated 1M NaOAC (adjusted to pH 5.0 with HOAC) to each tube. Purge and cap under N_2 . Shake for five hours. Centrifuge. Pour off supernatant. Purge with N_2 . Add 8 mL of deoxygenated DDW. Purge and cap under N_2 . Shake to resuspend the pellet. Centrifuge. Pour off and discard the supernatant. Purge and cap under N_2 .

5. Third Extraction: Fe-Mn Bound Zinc

Add 20 mL of 0.04 M $NH_2OH \cdot HCl$ in 25% v/v HOAC to each tube. Purge and cap under N_2 . Place in a hot water bath ($96 \pm 3^\circ C$) for six hours. Shake occasionally. Crack open the tubes a little after they begin to warm to prevent pressure buildup. Remove the tubes. Centrifuge. Pour off supernatant into pre-weighed vials. Wash the pellet with 8 mL of DDW as before. Recentrifuge and discard the wash. Reweigh the vials. N_2 atmosphere is not necessary from now on.

Extraction 4: Organically Bound Zinc

Add 3 mL of 0.02 M HNO_3 and 5 mL of 30% H_2O_2 (adjusted to pH 2 with HNO_3) to each tube. Heat at 85°C for three hours. Shake occasionally. Add an additional 3 mL of 30% H_2O_2 (pH 2 with HNO_3). Heat for three more hours, shaking intermittently. Let cool. Add 5 mL of 3.2 M NH_4OAC in 20% v/v HNO_3 . Dilute to about 20 mL with DDW. Shake for 30 minutes on shaker. Centrifuge the tubes. Pour the supernatant into pre-weighed vials. Weigh vials to determine the volume of supernatant. Wash the pellet as before.

Extraction 5: Residual Zinc

To residue of Extraction 4, add 5 mL of concentration HNO_3 . Heat in a hot water bath to near-dryness. Add an additional 5 mL and again heat to near-dryness. Dilute to 20 mL with 0.1 N HNO_3 . Spin down and pour supernatant into vials.

REAGENTS REQUIRED

<u>Reagent</u>	<u>Quantity</u>
1. 0.1 N HNO_3	2 L
2. 1 M MgCl_2 , pH 7.0	1 L
3. 1 M NaOAc , pH 5.0 with HNO_3	1 L
4. 0.04 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ in 25% v/v HOAc	2 L
5. 0.02 M HNO_3	1 L
6. 30% H_2O_2 , pH 2.0 with HNO_3	
7. 3.2 M NH_4OAc in 20% v/v HNO_3	1 L

APPENDIX 2

**Concentrations of Zinc, Zinc-65 and the
Specific Activity of Zinc-65 in Tubificids
Exposed to Water (Control) and Sediments
Labelled with Zinc-65**

CONCENTRATION OF ZINC AND ZINC-65 IN TUBIFICID WORMS

SAMPLE	SPECIES	WT. WORM+ STP(MG)	WT. OF STP(MG)	WT. OF WORMS MG	[ZN] IN EXTR. UG/L	VOLUME EXT. ML	[ZN] IN WORM UG/G	BQ IN 2 ML	BQ/G OF WORM	BQ/UG ZN WORM
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CONTROL EXPERIMENT

1	LIMNODRIL	42.1	32.5	9.6	540	4	225	2730	568750	2528
2	LIMNODRIL	43	30.7	12.3	550	4	179	2400	390244	2182
3	LIMNODRIL	38.9	30.5	8.4	400	4	190	2970	707143	3713
4	LIMNODRIL	41.8	31.9	9.9	400	4	162	2170	438384	2713
5	LIMNODRIL	46.9	33.2	13.7	590	4	172	3120	455474	2644
6	TUBIFEX	35.5	27.5	8	530	4	265	1060	265000	1000
7	TUBIFEX	37	28.8	8.2	490	4	239	670	163415	684
8	TUBIFEX	35.6	27.9	7.7	610	4	317	720	187013	590
9	TUBIFEX	35.1	25.9	9.2	520	4	226	1260	273913	1212
10	TUBIFEX	39	29.6	9.4	620	4	264	1040	221277	839

ONE MONTH EXPERIMENT

1-1	LIMNODRIL	51.7	31.3	20.4	1010	4	198	2	196	0.990
1-2	LIMNODRIL	35.2	24.8	10.4	490	4	188	2.08	400	2.122
1-3	LIMNODRIL	36.2	26.8	9.4	480	4	204	1.63	347	1.698
2-1	LIMNODRIL	43.6	28.6	15	870	4	232	2.76	368	1.586
2-2	LIMNODRIL	43.9	26.7	17.2	660	4	153	1.91	222	1.447
2-3	LIMNODRIL	38.3	28.5	9.8	560	4	229	2.15	439	1.920
3-1	LIMNODRIL	39.1	26.4	12.7	600	4	189	2.21	348	1.842
3-2	LIMNODRIL	39.7	29.1	10.6	470	4	177	1.88	355	2.000
3-3	LIMNODRIL	47.6	36.1	11.5	580	4	202	0.94	163	0.810
4-1	LIMNODRIL	37.3	25.6	11.7	560	4	191	1.38	236	1.232
4-2	LIMNODRIL	33.5	26.5	7	310	4	177	1	286	1.613
4-3	LIMNODRIL	38.3	25.6	12.7	590	4	186	1.72	271	1.458
5-1	TUBIFEX	39.4	30	9.4	750	4	319	2.6	553	1.733
5-2	TUBIFEX	34.8	24.7	10.1	660	4	261	1.16	230	0.879
5-3	TUBIFEX	39.1	30.1	9	700	4	311	0.97	216	0.693
6-1	TUBIFEX	33.7	24	9.7	590	4	243	1.22	252	1.034
6-2	TUBIFEX	40.5	30.8	9.7	670	4	276	2.11	435	1.575
6-3	TUBIFEX	33	25.2	7.8	640	4	328	1.77	454	1.383
9-1	TUBIFEX	39.7	28.2	11.5	760	4	264	2.67	464	1.757
9-2	TUBIFEX	34.6	25.1	9.5	740	4	312	1.47	309	0.993
9-3	TUBIFEX	39	28.4	10.6	620	4	234	0.98	185	0.790
10-1	TUBIFEX	40.2	31.1	9.1	630	4	277	2.84	624	2.254
10-2	TUBIFEX	36.7	27.6	9.1	660	4	290	1.97	433	1.492
10-3	TUBIFEX	44.3	34.1	10.2	780	4	306	2.91	571	1.865
11-1	TUBIFEX	32.8	24.4	8.4	660	4	314	2.04	486	1.545
11-2	TUBIFEX	35.6	29.6	6	420	4	280	1.13	377	1.345
11-3	TUBIFEX	38.6	32.8	5.8	550	4	379	1.8	621	1.636
12-1	TUBIFEX	39	29.7	9.3	740	4	318	1.58	340	1.068
12-2	TUBIFEX	34.4	24.5	9.9	820	4	331	1.77	358	1.079
12-3	TUBIFEX	42.1	32.5	9.6	720	4	300	0.96	200	0.667

AVERAGE

256 2 358 1.417

SAMPLE	WT. WORM+ STP(MG)	WT. OF STP(MG)	WT. OF WORM MG	[ZN] IN EXTR. UG/L	VOLUME EXT. ML	[ZN] IN WORM UG/G	BQ IN 2 ML	BQ/G OF WORM	BQ/UG ZN WORM
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TWO MONTH EXPERIMENT

13-1	LIMNODRIL	38.4	30.7	7.7	240	4	125	0.49	127	1.021
13-2	LIMNODRIL	40	28.9	11.1	470	4	169	-0.3		
13-3	LIMNODRIL	27.1	22.5	4.6	240	4	209	0.94	409	1.958
14-1	LIMNODRIL	43.3	27.1	16.2	870	4	215	1.67	206	0.960
14-2	LIMNODRIL	33.1	20.1	13	670	4	206	1.71	263	1.276
15-1	LIMNODRIL	30.8	20.2	10.6	670	4	253	0.94	177	0.701
15-2	LIMNODRIL	37.6	26.8	10.8	780	4	289	1.19	220	0.763
16-1	LIMNODRIL	30.9	20.8	10.1	640	4	253	1.77	350	1.383
16-2	LIMNODRIL	39.5	28.3	11.2	710	4	254	1.87	334	1.317
16-3	LIMNODRIL	41.1	32.7	8.4	670	4	319	1.59	379	1.187
17-1	TUBIFEX	28.1	25	3.1	270	4	348	-0.3		
19-1	TUBIFEX	28.9	22.8	6.1	440	4	289	2.55	836	2.898
20-1	TUBIFEX	27.8	25	2.8	270	4	386	-0.3		
7-1	TUBIFEX	28	21.8	6.2	420	4	271	0.99	319	1.179
8-1	TUBIFEX	33.5	27.7	5.8	440	4	303	-0.3		

AVERAGE

259 329 1.331

APPENDIX 3

Chemical Partitioning of Zinc in Sediments From the One-Month Tubificid Exposure Experiment

FIRST HARVEST SEDIMENT EXTRACTS - FINAL VERSION

SAMPLE	EXCHANGEABLE ZINC ug/g	PERCENT OF TOTAL	CARBONATE BOUND ZINC ug/g	PERCENT OF TOTAL	Fe-Mn BOUND ZINC ug/g	PERCENT OF TOTAL	ORG. BOUND ZINC ug/g	PERCENT OF TOTAL	RESIDUAL ZINC ug/g	PERCENT OF TOTAL	TOTAL DIG. (Aqua Regia) ug/g	SUM OF FRACTIONS ug/g	FRACTION OF TOTAL %	INTERSTITIAL WATER mg/L
1B S1	0.3	0.08	93	26.32	210	59.44	21	5.94	29	8.21	370	353.3	4.5	0.04
1B S2	0.4	0.11	132	35.54	204	54.93	19	5.12	16	4.31	400	371.4	7.2	0.03
2B S1	0.1	0.02	80	19.09	290	69.20	25	5.97	24	5.73	410	419.1	-2.2	0.07
2B S2	0.1	0.03	67	17.44	240	62.48	25	6.51	52	13.54	380	384.1	-1.1	0.04
3B S1	0.4	0.11	104	27.48	220	58.14	21	5.55	33	8.72	400	378.4	5.4	0.08
3B S2	0.2	0.05	89	24.37	220	60.24	23	6.30	33	9.04	400	365.2	8.7	0.08
4B S1	0.1	0.03	87	25.06	210	60.50	23	6.63	27	7.78	400	347.1	13.2	0.04
4B S2	0.1	0.03	100	25.18	220	55.40	22	5.54	55	13.85	410	397.1	3.1	0.02
5A S1	0.3	0.08	112	31.43	200	56.13	21	5.89	23	6.46	390	356.3	8.6	0.06
5A S2	0.2	0.06	103	29.41	200	57.11	21	6.00	26	7.42	420	350.2	16.6	0.08
6A S1	0.3	0.09	111	32.81	182	53.80	18	5.32	27	7.98	380	338.3	11.0	0.03
6A S2	0.2	0.05	94	25.60	220	59.91	23	6.26	30	8.17	410	367.2	10.4	0.03
9A S1	0.1	0.03	77	23.19	200	60.22	22	6.62	33	9.94	410	332.1	19.0	0.05
9A S2	0.1	0.03	90	23.93	220	58.50	23	6.12	43	11.43	400	376.1	6.0	0.07
10A S1	0.1	0.02	106	26.17	220	54.31	26	6.42	53	13.08	410	405.1	1.2	0.04
10A S2	0.1	0.03	108	30.16	198	55.29	22	6.14	30	8.38	360	358.1	0.5	0.04
11A S1	0.2	0.06	103	29.41	197	56.25	22	6.28	28	8.00	390	350.2	10.2	0.04
11A S2	0.4	0.11	123	34.61	191	53.74	20	5.63	21	5.91	410	355.4	13.3	0.04
12A S1	0.3	0.08	110	30.36	200	55.20	23	6.35	29	8.00	370	362.3	2.1	0.03
12A S2	0.3	0.09	95	29.11	182	55.78	20	6.13	29	8.89	380	326.3	14.1	0.05
21 S1	0.6	0.16	120	32.12	195	52.19	21	5.62	37	9.90	380	373.6	1.7	0.03
21 S2	0.4	0.10	92	23.81	220	56.94	24	6.21	50	12.94	360	386.4	-7.3	0.03
AVERAGE	0.2	0.07	100	27.39	211	57.53	22	6.02	33	8.98	393	366	6.6	0.05

APPENDIX 4

Chemical Partitioning of Zinc in Sediments From the Two-Month Tubificid Exposure Experiment

SECOND HARVEST SEDIMENT EXTRACTS-FINAL VERSION

SAMPLE	EXCHANGEABLE ZINC ug/g	PERCENT OF TOTAL %	CARBONATE BOUND ZINC ug/g	PERCENT OF TOTAL	Fe-Mn BOUND ZINC ug/g	PERCENT OF TOTAL	ORG. BOUND ZINC ug/g	PERCENT OF TOTAL	RESIDUAL ZINC ug/g	PERCENT OF TOTAL	TOTAL DIB. (Aqua Regia) ug/g	SUM OF FRACTIONS ug/g	FRACTION OF TOTAL %	INTERSTITIAL WATER ug/L
7S1	1.4	0.37	131	34.53	165	43.49	22	5.90	60	15.81	390	379	2.72	0.049
7S2	0.47	0.12	143	35.96	164	42.52	24	6.04	61	15.35	392	397	-1.40	0.043
8S1	1.4	0.36	150	38.13	164	41.69	21	5.34	57	14.49	399	393	1.40	0.019
8S2	1.4	0.36	132	34.07	172	44.40	22	5.68	60	15.49	392	387	1.17	0.019
13S1	4.1	0.87	195	41.57	183	39.01	25	5.33	62	13.22	471	459	0.40	0.074
13S2	3	0.80	152	40.64	148	38.57	22	5.88	49	13.10	375	374	0.27	0.069
14S1	1.6	0.41	140	36.21	159	41.13	28	7.24	58	15.00	397	387	2.62	0.161
14S2	2.3	0.57	141	35.14	169	42.11	24	5.98	65	16.20	392	401	-2.37	0.127
15S1	1.6	0.40	156	39.43	160	40.44	24	6.07	54	13.65	373	396	-6.06	0.015
15S2	1.2	0.30	147	37.01	166	41.79	25	6.29	56	14.60	381	397	-4.25	0.051
16S1	1.6	0.44	162	40.02	164	40.51	25	6.18	52	12.85	395	405	-2.48	0.079
16S2	1.9	0.50	162	42.42	148	38.75	25	6.55	45	11.78	394	382	3.07	0.059
17S1	1.4	0.37	142	37.53	154	40.70	28	7.40	53	14.01	379	378	0.16	0.027
17S2	0.79	0.14	187	34.07	231	42.09	48	8.75	82	14.94	360	549	-44.42	0.033
18S1	1.2	0.28	164	38.48	174	40.83	30	7.04	57	13.37	409	426	-4.21	0.033
18S2	0.61	0.15	156	38.46	170	41.91	30	7.40	49	12.08	385	406	-5.35	0.022
19S1	0.75	0.19	149	37.09	170	42.31	33	8.21	49	12.20	412	402	2.49	0.033
19S2	0.49	0.12	153	37.55	169	41.47	31	7.61	54	13.25	398	407	-2.38	0.027
20S1	1.9	0.48	154	39.20	156	39.70	36	9.16	45	11.45	396	393	0.78	0.027
20S2	0.67	0.22	123	31.31	179	45.56	32	8.15	58	14.76	338	393	-16.23	0.033
22S1	1	0.25	156	39.00	166	41.50	27	6.75	50	12.50	401	400	0.25	0.076
22S2	0.78	0.20	154	39.21	158	40.23	36	9.17	44	11.20	384	393	-2.29	0.058
AVERAGE	1.5	0.36	152	37.59	168	41.44	28	6.91	56	13.70	392	405	-3.46	0.052

APPENDIX 5

Zinc-65 in Sediments from the One-Month Tubificid Exposure

ONE MONTH EXPOSURE SEDIMENT EXTRACTS

SAMPLE	EXCHANGEABLE ZINC ug/g	ZN-65 IN FRACTION BQ/G	SPECIFIC ACTIVITY BQ/UG	CARBONATE BOUND ZINC ug/g	ZN-65 IN FRACTION BQ/G	SPECIFIC ACTIVITY BQ/UG	Fe-Mn BOUND ZINC ug/g	ZN-65 IN FRACTION BQ/G	SPECIFIC ACTIVITY BQ/UG	ORG. BOUND ZINC ug/g	ZN-65 IN FRACTION BQ/G	SPECIFIC ACTIVITY BQ/UG
1B S1	0.3	3.26	10.870	93	469	5.04	210	228	1.085	21	14.62	0.696
1B S2	0.4	3.33	8.333	132	370	2.80	204	189	0.929	19	12.49	0.657
2B S1	0.1	3.33	33.333	80	573	7.16	290	436	1.505	25	35.23	1.409
2B S2	0.1	-1.50	-15.000	67	412	6.15	240	296	1.232	25	10.20	0.408
3B S1	0.4	2.40	6.000	104	502	4.83	220	220	1.000	21	7.92	0.377
3B S2	0.2	-1.88	-9.375	89	488	5.49	220	239	1.088	23	-4.21	-0.183
4B S1	0.1	1.00	10.000	87	494	5.68	210	227	1.081	23	-4.60	-0.200
4B S2	0.1	-1.50	-15.000	100	524	5.24	220	206	0.937	22	3.93	0.179
5A S1	0.3	2.61	8.696	112	512	4.57	200	191	0.954	21	-5.16	-0.246
5A S2	0.2	1.67	8.333	103	517	5.02	200	218	1.092	21	-4.63	-0.221
6A S1	0.3	3.33	11.111	111	463	4.17	182	147	0.810	18	7.57	0.420
6A S2	0.2	-1.58	-7.895	94	515	5.47	220	209	0.950	23	2.73	0.119
9A S1	0.1	-2.14	-21.429	77	427	5.55	200	203	1.014	22	3.88	0.176
9A S2	0.1	2.50	25.000	90	475	5.28	220	189	0.858	23	11.50	0.500
10A S1	0.1	1.43	14.286	106	521	4.92	220	184	0.838	26	15.21	0.585
10A S2	0.1	-2.14	-21.429	108	508	4.70	198	151	0.764	22	9.63	0.438
11A S1	0.2	2.14	10.714	103	497	4.82	197	183	0.929	22	11.45	0.5211
11A S2	0.4	-2.86	-7.143	123	529	4.30	191	204	1.070	20	16.25	0.813
12A S1	0.3	2.61	8.696	110	491	4.46	200	249	1.246	23	10.20	0.444
12A S2	0.3	2.50	8.333	95	334	3.52	182	191	1.051	20	-6.52	-0.326
21 S1	0.6			120			195			21		
21 S2	0.4			92			220			24		

SAMPLE	RESIDUAL ZINC ug/g	ZN-65 IN FRACTION BQ/G	SPECIFIC ACTIVITY BQ/UG	TOTAL DIG. (Aqua Regia) ug/g	ZN-65 IN FRACTION BQ/G	SPECIFIC ACTIVITY BQ/UG	INTERSTITIAL WATER mg/L	SPECIFIC ACTIVITY BQ/UG
1B S1	29	9.52	0.328	370	756	2.04	0.04	-3.8
1B S2	16	-8.28	-0.517	400	712	1.78	0.03	5.0
2B S1	24	1.32	0.055	410	633	1.54	0.07	2.9
2B S2	52	-3.55	-0.068	380	575	1.51	0.04	3.8
3B S1	33	3.67	0.111	400	500	1.25	0.08	2.5
3B S2	33	-4.58	-0.139	400	711	1.78	0.08	-1.9
4B S1	27	-4.94	-0.183	400	661	1.65	0.04	-3.8
4B S2	55	12.10	0.220	410	752	1.83	0.02	5.0
5A S1	23	-5.48	-0.238	390	669	1.71	0.06	-2.5
5A S2	26	2.28	0.088	420	718	1.71	0.08	5.0
6A S1	27	-6.43	-0.238	380	628	1.65	0.03	-5.0
6A S2	30	1.91	0.064	410	683	1.67	0.03	5.0
9A S1	33	2.42	0.073	410	737	1.80	0.05	3.0
9A S2	43	-5.33	-0.124	400	679	1.70	0.07	-2.1
10A S1	53	3.38	0.064	410	678	1.65	0.04	-3.8
10A S2	30	-5.36	-0.179	360	653	1.81	0.04	-3.8
11A S1	28	2.77	0.099	390	735	1.88	0.04	6.3
11A S2	21	-6.56	-0.313	410	718	1.75	0.04	-3.8
12A S1	29	13.90	0.480	370	666	1.80	0.03	3.3
12A S2	29	-6.90	-0.238	380	609	1.60	0.05	-3.0
21 S1	37			380			0.03	-5.0
21 S2	50			360			0.03	8.3

APPENDIX 6

Zinc-65 in Sediments from the Two-Month Tubificid Exposure

TWO MONTH EXPOSURE SEDIMENT EXTRACTS

SAMPLE	SAMPLE	EXCHANGEABLE ZINC ug/g	EXCHANGEABLE ZINC IN EXTRACT ug/ml	ACTIVITY OF FRACTION BO/ZHL (BASED ON RECOUNTS)	ZN-65 IN FRACTION BO/G	SPECIFIC ACTIVITY BO/UG ZINC (BASED ON RECOUNTS)	CARBONATE BOUND ZINC ug/g	CARBONATE BOUND ZINC IN EXTRACT ug/ml	ACTIVITY OF FRACTION BO/ZHL	ZN-65 IN FRACTION BO/G	SPECIFIC ACTIVITY BO/UG ZINC
751	751	1.4	0.102		0.0	0.00	131	9.5	77	529	4.05
752	752	0.97	0.063	1.6	12.3	12.70	143	9.3	66	508	3.55
851	851	1.4	0.075		0.0	0.00	150	8	64	598	4.00
852	852	1.4	0.1	1.2	8.2	6.00	132	9.6	66	453	3.44
1351	1351	4.1	0.128		0.0	0.00	195	6.1	43	688	3.52
1352	1352	3	0.128		0.0	0.00	152	6.6	46	530	3.48
1451	1451	1.6	0.097	1.8	14.8	9.28	140	8.5	58	478	3.41
1452	1452	2.3	0.15		0.0	0.00	141	9.4	51	383	2.71
1551	1551	1.6	0.072		0.0	0.00	156	7	47	522	3.36
1552	1552	1.2	0.069	-0.3			147	8.4	46	404	2.74
1651	1651	1.8	0.08		0.0	0.00	162	7.1	38	433	2.68
1652	1652	1.9	0.069		0.0	0.00	162	5.9	24.3	333	2.06
1751	1751	1.4	0.089		0.0	0.00	142	9	56	443	3.11
1752	1752	0.79	0.038		0.0	0.00	187	9	60	622	3.33
1851	1851	1.2	0.066		0.0	0.00	164	9.1	52	467	2.86
1852	1852	0.61	0.03		0.0	0.00	156	7.7	46	467	2.99
1951	1951	0.75	0.038		0.0	0.00	149	7.6	50	490	3.29
1952	1952	0.49	0.025		0.0	0.00	153	7.8	58	570	3.72
2051	2051	1.9	0.105		0.0	0.00	154	8.4	46	422	2.74
2052	2052	0.87	0.072	1.8	10.8	12.50	123	10.2	48	289	2.35
2251	2251	1	0.049				156	7.6			
2252	2252	0.78	0.038				154	7.5			

TWO MONTH EXPOSURE SEDIMENT EXTRACTS

SAMPLE	Fe-Mn BOUND ZINC ug/g	Fe-Mn BOUND ZINC IN EXTRACT ug/ml	ACTIVITY OF FRACTION BQ/2ML	VOLUME OF EXTRACT ML	ZN-65 IN FRACTION BQ/G	SPECIFIC ACTIVITY BQ/UG ZINC	ORG. BOUND ZINC ug/g	ORG. BOUND ZINC IN EXTRACT ug/ml	ACTIVITY OF FRACTION BQ/2ML	VOLUME OF EXTRACT ML	ZN-65 IN FRACTION BQ/G	SPECIFIC ACTIVITY BQ/UG ZINC
7S1	165	4.6	9.6	20.9	172	1.04	22	0.68	1.07	18.8	17.3	0.79
7S2	169	4.2	9.6	20.9	193	1.14	24	0.65	-0.3	18.9		
8S1	164	3.6	12.1	19.5	276	1.68	21	0.46	1.09	19.9	25.3	1.18
8S2	172	5.1	9.3	19.7	157	0.91	22	0.7	1.04	18.6	16.6	0.74
13S1	183	2.3	4.8	19.9	191	1.04	25	0.32	-0.3	19.2		
13S2	148	2.6	7.4	19.7	210	1.42	22	0.4	-0.3	19.7		
14S1	159	4	11.3	19.3	225	1.41	28	0.72	0.98	19	19.2	0.68
14S2	169	4.6	9.7	19.6	178	1.05	24	0.68	1.19	19.1	21.3	0.87
15S1	160	2.9	7.4	19.8	204	1.28	24	0.46	0.42	19	11.1	0.46
15S2	166	3.9	6	19.4	128	0.77	25	0.63	0.71	18.4	14.3	0.56
16S1	164	2.9	6.6	19.8	186	1.14	25	0.46	1.45	19.1	39.5	1.58
16S2	148	2.3	5.3	18.8	171	1.15	25	0.37	-0.3	19.6		
17S1	154	4	7.8	19.5	150	0.98	28	0.72	1.32	19.3	25.2	0.92
17S2	231	4.3	8.7	20.7	233	1.01	48	0.96	1.19	19.3	29.8	0.62
18S1	174	4	8.2	19.4	179	1.03	30	0.72	-0.3	18.8		
18S2	170	3.4	6.3	19.7	157	0.93	30	0.63	-0.3	18.9		
19S1	170	3.6	5.7	19.3	135	0.79	33	0.7	1.76	19.4	41.8	1.26
19S2	169	3.5	10.4	19.4	248	1.49	31	0.65	1.04	19.2	24.5	0.80
20S1	156	3.6	6	18.9	130	0.83	36	0.82	-0.3	19.2		
20S2	179	6.3	4.6	18.9	65	0.37	32	1.16	-0.3	18.6		
22S1	166	3.3		19.6			27	0.54		19.2		
22S2	158	3		20.5			36	0.75		18.6		

TWO MONTH EXPOSURE SEDIMENT EXTRACTS

SAMPLE	RESIDUAL ZINC ug/g	RESIDUAL ZINC IN EXTRACT ug/ml	ACTIVITY OF FRACTION BQ/2ML	ZN-65 IN FRACTION BQ/G	SPECIFIC ACTIVITY BQ/UG ZINC	TOTAL DIG. (Aqua Regia) ug/g	TOTAL DIG. (Aqua Regia) IN EXTRACT ug/ml	ACTIVITY OF FRACTION BQ/2ML	ZN-65 IN FRACTION BQ/G	SPECIFIC ACTIVITY BQ/UG ZINC	INTERSTITIAL WATER mg/L	INTERSTITIAL ACTIVITY BQ/2ML	SPECIFIC ACTIVITY BQ/UG ZINC
7S1	60	1.76	2.76	47.4	0.78	390	6.6	28.5	646	2.16	0.049	-0.3	
7S2	61	1.59	-0.3			392	7.4	22	582	1.49	0.043	-0.3	
8S1	57	1.19	0.59	13.8	0.25	399	9.3	35	751	1.88	0.019	-0.3	
8S2	60	1.74	-0.3			392	7.7	28.3	720	1.84	0.019	-0.3	
13S1	62	0.78	-0.3			471	5.7	21.6	893	1.89	0.074	-0.3	
13S2	49	0.85	1.55	44.7	0.91	375	6.2	22.7	686	1.83	0.069	2.49	18.04
14S1	58	1.41	1.73	35.7	0.61	397	8.3	30.4	727	1.83	0.161	-0.3	
14S2	65	1.72	-0.3			392	7.2	19.3	526	1.34	0.127	0.51	2.01
15S1	54	0.97	-0.3			373	6.8	17	466	1.25	0.015	1.97	65.67
15S2	58	1.32	-0.3			381	9.8	28.6	556	1.46	0.051	-0.3	
16S1	52	0.91	-0.3			395	10.4	26.4	502	1.27	0.079	-0.3	
16S2	45	0.66	-0.3			394	7.7	22.9	586	1.49	0.059	0.4	3.39
17S1	53	1.33	-0.3			379	7.2	22.9	603	1.59	0.027	-0.3	
17S2	82	1.59	1.7	44.0	0.53	380	14.7	47	608	1.60	0.033	-0.3	
18S1	57	1.27	0.88	19.8	0.35	409	6.9	31.3	929	2.27	0.033	2.34	35.45
18S2	49	0.96	0.62	15.7	0.32	385	9.8	29.5	580	1.51	0.022	-0.3	
19S1	49	1	1.67	40.9	0.84	412	8.4	15.5	380	0.92	0.033	2.06	31.21
19S2	54	1.09	-0.3			398	7.6	37	969	2.43	0.027	0.8	14.81
20S1	45	0.99	-0.3			396	5.4	29.9	1095	2.77	0.027	2.2	40.74
20S2	58	1.91	-0.3			338	17.4	24.5	238	0.70	0.033	-0.3	
22S1	50	0.97				401	10				0.076		
22S2	44	0.86				384	6.2				0.058		

APPENDIX 7

Chemical Fractionation of Zinc with Depth in Two Cores from Toronto Harbour

ZINC CONCENTRATION DISTRIBUTION BY SEDIMENT DEPTH AND FRACTION

DEPTH cm	EXCHANGEABLE ZINC ug/g	CARBONATE BOUND ZINC ug/g	PERCENT OF TOTAL	Fe-Mn BOUND ZINC ug/g	PERCENT OF TOTAL	ORG. BOUND ZINC ug/g	PERCENT OF TOTAL	RESIDUAL ZINC ug/g	PERCENT OF TOTAL	TOTAL DIG. (Aqua Regia) ug/g	SUM OF FRACTIONS ug/g	FRACTION OF TOTAL %	INTERSTITIAL WATER mg/L	POROSITY %
Core No. 1														
0-1	-0.3	61	17.6	215	61.9	18.2	5.2	53	15.3	431	348	19.4	77	69.8
1-2	-0.3	113	33.4	157	46.4	18.8	5.6	49	14.5	405	338	16.5	54	65.8
2-3	-0.3	106	26.9	217	55.2	19.1	4.9	51	13.0	432	393	8.9	74	64.2
3-4	-0.3	82	22.5	218	59.7	17.8	4.9	47	12.9	455	365	19.8	106	64.7
4-5	-0.3	72	17.8	254	62.7	24	5.9	55	13.6	425	405	4.6	151	63.6
5-6	-0.3	156	33.1	247	52.4	21	4.5	47	10.0	438	471	-7.6	152	59.9
6-7	-0.3	44	12.3	250	69.8	19	5.3	45	12.6	432	358	17.1	171	60.5
7-8	-0.3			287		13.2		57		442			113	59.6
8-9	-0.3	35	8.7	292	72.6	25	6.2	50	12.4	463	402	13.1	143	57.5
9-10	-0.3	50	12.6	262	65.9	27	6.8	58	14.6	337	397	-17.9	128	58.3
11-12	-0.3	38	9.3	295	71.9	24	5.8	53	12.9	462	410	11.2	164	53.7
AVERAGE	-0.3	75.7	19.4	245	61.8	20.6	5.5	51	13.2	429	389	8.5	121	61.6
Core No. 2														
0-1	-0.3	97	26.4	196	53.3	18.6	5.1	56	15.2	362	368	-1.6	109	75.7
1-2	-0.3	79	23.3	186	54.8	17.9	5.3	56	16.5	398	339	14.8	94	64.6
2-3	-0.3	54	13.3	272	67.1	23	5.7	56	13.8	424	405	4.4	112	64.2
3-4	-0.3	87	21.1	244	59.2	23	5.6	58	14.1	470	412	12.3	137	62.7
4-5	-0.3	41	10.7	267	69.5	23	6.0	53	13.8	467	384	17.7	102	61.1
5-6	-0.3	64	15.6	268	65.3	24	5.8	54	13.2	427	410	3.9	88	60.1
6-7	-0.3	15.6	3.8	306	74.8	30	7.3	57	13.9	459	409	10.9	93	59.6
7-8	-0.3	44	11.9	259	69.9	21	5.7	46	12.4	447	370	17.2	85	58.5
8-9	-0.3	32	8.1	282	71.0	26	6.5	57	14.3	443	397	10.3	94	56.1
9-10	-0.3	25	6.8	268	72.8	25	6.8	50	13.6	400	368	7.9	105	55.5
11-12	-0.3	19.5	5.2	273	73.4	26	7.0	53	14.3	424	372	12.3	102	53.2
13-14	-0.3	40	10.9	247	67.4	25	6.8	54	14.7	427	366	14.2	135	50.6
AVERAGE	-0.3	49.8	13.1	256	66.5	23.5	6.1	54	14.2	429	384	10.4	105	60.2

APPENDIX 8

Zinc-65 Activity and Zinc Content of Chemical Fractions in the Zinc-65 Exchange Experiment

EXCHANGE EXPERIMENT - SUMMARY OF THE DATA

SAMPLE	EXCH-ANGIBLE ZINC BQ/G	PERCENT OF TOTAL ZINC %	ZN-65 IN FRACTION BQ/G	PERCENT OF TOTAL ACTIVITY %	MEAN OF A AND B BQ/G	LOG (ZN-65) IN FRACTION	SPECIFIC ACTIVITY BQ/G	MEAN OF A AND B
1A	0.39	0.15		0.00				
1B	0.31	0.06	7.66	0.84	7.66	0.8842046428	25.00	25.00
2A	0.4	0.10		0.00				
2B	0.23	0.06		0.00				
3A	0.42	0.10	10.39	1.53	10.39	1.0165992618	25.00	25.00
3B	0.43	0.10		0.00				
4A	0.49	0.11		0.00				
4B	0.26	0.06		0.00				
5A	0.53	0.13	10.90	1.58	10.90	1.0373687499	20.43	20.43
5B	0.36	0.09		0.00				
6A	0.55	0.16		0.00				
6B	0.32	0.08		0.00				
7A	0.58	0.13		0.00				
7B	0.39	0.10		0.00				
8A	0.75	0.18		0.00				
8B	0.47	0.12		0.00				
9A	1.5	0.61	12.74	2.67	12.74	1.1050439079	5.12	5.12
9B	1.7	0.45		0.00				
10A	4.5	1.21	16.24	2.98	13.30	1.1237900566	3.34	2.84
10B	4.9	1.17	10.36	1.51			2.35	
11A	5.2	1.58	20.93	3.03	12.63	1.1013042023	3.39	2.11
11B	5.2	1.41	4.32	0.57			0.83	

EXCHANGE EXP

SAMPLE	CARBONATE BOUND ZINC ug/g	PERCENT OF TOTAL ZINC %	ZN-65 IN FRACTION BQ/G	PERCENT OF TOTAL ACTIVITY %	MEAN OF A AND B	LOG (ZN-65) IN FRACTION	SPECIFIC ACTIVITY BQ/UG	MEAN OF A AND B
1A	150	38.04	514.47	62.5	555.1	2.7443767564	2.86	3.33
1B	157	32.69	595.74	65.3			3.80	
2A	165	39.29	520.00	66.9	463.6	2.6661774909	3.15	2.92
2B	151	39.72	407.27	56.6			2.69	
3A	154	35.12	384.42	56.6	459.8	2.6625371546	2.50	3.00
3B	153	37.02	535.12	60.7			3.51	
4A	157	36.10	319.15	52.4	389.6	2.5905904864	2.03	2.61
4B	144	35.61	460.00	59.5			3.19	
5A	162	38.94	394.20	57.1	461.4	2.6640453167	2.43	2.88
5B	159	39.94	528.53	82.1			3.33	
6A	174	41.95	419.35	85.2	440.9	2.6443671065	2.41	2.72
6B	152	39.00	462.50	83.3			3.03	
7A	161	37.40	595.30	80.7	568.8	2.75498751	3.70	3.96
7B	129	33.85	542.37	81.5			4.21	
8A	164	39.79	483.22	81.7	481.4	2.6825120912	2.95	3.20
8B	139	35.60	479.59	72.2			3.46	
9A	161	39.16	447.76	72.9	485.7	2.6863670116	2.79	3.30
9B	138	36.17	523.64	72.4			3.83	
10A	147	36.35	368.63	67.7	456.1	2.6590371558	2.50	3.15
10B	143	37.87	543.52	79.1			3.81	
11A	157	39.89	523.36	75.9	551.1	2.7412296936	3.33	3.68
11B	143	38.69	578.83	77.0			4.04	

EXCHANGE EXP

SAMPLE	Fe-Mn BOUND ZINC ug/g	PERCENT OF TOTAL ZINC %	ZN-65 IN FRACTION BQ/G	PERCENT OF TOTAL ACTIVITY %	MEAN OF A AND B	LOG (ZN-65) IN FRACTION	SPECIFIC ACTIVITY BQ/UG	MEAN OF A AND B
1A	206	43.5	308.22	37.5	291.59	2.4647720955	1.50	1.39
1B	214	44.6	274.96	30.1			1.28	
2A	178	42.4	257.40	33.1	284.70	2.4543874671	1.44	1.72
2B	156	41.0	312.00	43.4			2.00	
3A	194	44.2	276.31	40.7	306.21	2.4860160842	1.42	1.68
3B	173	41.9	336.10	38.2			1.94	
4A	190	43.7	290.27	47.6	299.82	2.4768612933	1.53	1.63
4B	178	44.0	309.38	40.0			1.74	
5A	171	41.1	285.51	41.3	200.27	2.3016210849	1.67	1.18
5B	157	41.9	115.04	17.9			0.69	
6A	167	40.3	73.02	14.8	82.92	1.9186400747	0.43	0.50
6B	162	41.6	92.81	16.7			0.57	
7A	183	42.5	129.83	17.6	126.36	2.1015952559	0.71	0.72
7B	169	44.3	122.88	18.5			0.73	
8A	170	41.2	76.23	12.9	111.73	2.0481554346	0.45	0.66
8B	168	43.0	147.22	22.2			0.88	
9A	166	40.4	153.58	25.0	164.10	2.2151089401	0.93	1.01
9B	160	41.9	174.62	24.2			1.09	
10A	168	41.5	159.98	29.4	146.79	2.1667108698	0.95	0.92
10B	151	40.0	133.61	19.4			0.89	
11A	151	38.4	145.58	21.1	157.25	2.1965964519	0.86	0.98
11B	144	39.0	168.92	22.5			1.10	

EXCHANGE EPH

SAMPLE	PERCENT ZINC -g/g	PERCENT OF TOTAL ZINC %	ZN-65 IN FRACTION 20/G	SPECIFIC ACTIVITY 20/GS	RESIDUAL ZINC ug/g	PERCENT OF TOTAL ZINC %	ZN-65 IN FRACTION 20/G	PERCENT OF TOTAL ACTIVITY %	MEAN OF A AND B	LOG (ZN-65) IN FRACTION	SPECIFIC ACTIVITY 20/GS	MEAN OF A AND B
1A	31.6	6.62	-9.21	-0.29	55	11.62		0.00				
1B	41.8	8.72	-5.97	-0.14	67	13.95	34.47	3.78	34.47	1.5374171566	0.51	0.51
1A	29.8	7.05	-9.55	-0.33	47	11.19		0.00				
2B	26.0	6.83	-10.53	-0.41	47	12.36		0.00				
3A	31.1	7.32	-7.40	-0.23	58	13.23	7.79	1.15	8.75	0.9417397204	0.14	0.15
3B	30.8	6.67	-9.43	-0.26	51	12.34	9.70	1.10			0.18	
4A	34.4	7.40	-7.58	-0.22	53	12.19		0.00				
4B	30.1	7.44	-7.05	-0.23	52	12.86	3.75	0.49	3.75	0.5740312677	0.07	0.07
5A	30.4	7.32	-8.30	-0.27	52	12.50		0.00				
5B	25.8	6.47	-8.78	-0.34	46	11.55		0.00				
6A	25.1	6.06	-11.43	-0.46	48	11.57		0.00				
6B	27.5	7.05	-8.77	-0.32	48	12.31		0.00				
7A	29.9	6.95	-7.48	-0.25	56	13.01	12.53	1.70	12.53	1.0980424634	0.22	0.22
7B	25.7	7.54	-6.07	-0.21	54	14.17		0.00				
8A	25.4	6.89	-8.46	-0.33	49	11.89	32.21	5.44	34.60	1.5391047225	0.56	0.58
8B	31.0	7.94	-7.39	-0.24	52	13.32	36.99	5.57			0.71	
9A	23.9	5.74	-5.94	-0.29	56	14.11		0.00				
9B	23.8	6.24	-5.10	-0.21	58	15.20	24.73	3.42	24.73	1.3931762189	0.43	0.43
10A	23.5	5.80	-5.50	-0.23	61	15.09		0.00				
10B	23.2	5.88	-6.05	-0.27	57	15.10		0.00				
11A	22.4	5.69	-6.59	-0.29	57	14.48		0.00				
11B	22.4	6.05	-5.99	-0.27	55	14.88		0.00				

EXCHANGE EXP

SAMPLE	TOTAL DIS. (Acid Regre) ug/g	ZN-65 IN FRACTION BQ/G	MEAN OF A AND B	LOG (ZN-65) IN FRACTION	SPECIFIC ACTIVITY BQ/UG	MEAN OF A AND B	TIME LOG(DAYS)	SUM OF ACTIVITY FRACTIONS BQ/G	MEAN OF A AND B BQ/G	LOG (ZN-65) IN FRACTION
1A	454	798.64	759.15	2.8803282616	1.74	1.61	-2.682	823	867.76	2.9383998978
1B	493	729.66			1.48		-2.682	913		
2A	431	669.12	748.92	2.8744374376	1.55	1.82	-2.204	777	748.34	2.8740968492
2B	398	828.73			2.08		-2.204	719		
3A	430	555.00	740.00	2.8692317197	1.29	1.65	-1.682	679	779.91	2.8920469455
3B	450	925.00			2.01		-1.682	881		
4A	442	623.76	617.61	2.7907169015	1.41	1.48	-1.301	609	691.27	2.8396478762
4B	395	611.46			1.55		-1.301	773		
5A	421	685.39	751.67	2.8760277884	1.63	1.81	-0.824	691	667.09	2.8241827253
5B	410	817.95			1.99		-0.824	644		
6A	414	616.87	572.55	2.757810869	1.49	1.40	-0.347	492	523.84	2.7192017667
6B	403	528.23			1.31		-0.347	555		
7A	476	755.45	676.98	2.8305737349	1.78	1.58	0.146	738	701.46	2.845002113
7B	402	558.50			1.39		0.146	665		
8A	436	469.70	656.13	2.8169928844	1.08	1.62	0.602	592	627.74	2.7977755111
8B	390	842.57			2.16		0.602	664		
9A	428	786.03	812.86	2.9100159819	1.84	1.99	1.079	614	668.53	2.8251213621
9B	393	839.69			2.14		1.079	723		
10A	399	533.80	493.92	2.6936555464	1.34	1.70	1.38	545	516.17	2.7896997847
10B	394	454.04			2.07		1.38	687		
11A	417	774.19	809.47	2.9082014035	1.86	2.03	1.519	690	720.98	2.857922197
11B	384	844.75			2.20		1.519	752		

APPENDIX 9

MOE Data for Correlation Analysis

MOE DATA

STATION	INTERST. WATER MG/L	F1 UG/G	F2 UG/G	F3 UG/G	F4 UG/G	RESIDUAL UG/G	TOTAL UG/G	SUMTOTAL UG/G	% DEVIATION	BIOTA	FE UG/G	% SAND
45	0.01	0.38	5.45	36.5	5.18	21.25	53.5	68.9	-28.8	133.04	17000	
46	0.01	1.18	14.75	135	6.15	26.75	190.5	183.5	3.7	124.97	58000	
47	0.01	1.3	16.5	125	5.72	22.25	159	170.5	-7.2	112.65	34000	
48	0.02	1.15	23.75	205	6.45	37.5	300	274	8.7	117.82	59000	
66	0.003	0.55	0.78	20.25	2.03	17.5	39.3	41.1	-4.6	82.94	8100	
157	0.003	0.73	3.25	21.5	17.75	104.5	312.5	148	52.6	165.88	16000	
160	0.003	0.68	1.8	76	4.2	35.9	234	118.5	49.4	129.24	9400	
183	0.003	1.2	4.53	345	24	86.65	224.5	461.5	-105.6	181.22	23000	
1346	0.145	2.42	11.92	435.8	21.18	49.9	567.3	521.2	8.1	190.41	17000	32.01
1352	0.145	4.51	10.29	411.9	10.79	27.6	477	465.1	2.5	208.49	31000	3.09
1354	0.125	1.28	11.84	429.1	40.12	9.9	597.3	486.9	18.5	288.47	26000	8.81
1357	0.125	1.92	10.25	373.1	15.95	22.3	538.2	423.5	21.3	175.49	31000	3.35
1362	0.127	1.18	6.36	354.1	5.74	88.7	425	456.1	-7.3	257.83	28000	3.24
1365	0.271	4	9.49	308.2	8.41	82.5	411	412.6	-0.4	237.29	30000	1.76
1366	0.217	4.91	10.57	408.1	8.08	2.8	478	434.4	9.1	280.15	31000	0.94
1371	0.07	1.17	6.5	344.2	6.37	10.9	397.3	369.2	7.1	239.73	29000	5.49
1379	0.036	1.73	3.84	240.9	3.15	32.7	267.9	282.3	-5.4	190.36	23000	9.1
2034	0.036	0.53	2.12	376.6	22.02	223.9	647.3	625.5	3.4	229.51	24000	25.45
2082	0.003	1.3	2.38	27	0.39	55.8	92.4	86.9	6.0	236.89	15000	26.29
2083	0.024	0.73	1.45	46.1	0.3	67.2	102.3	115.8	-13.2	61.82	23000	17.05
2097	0.072	11.46	17.71	108.1	8.88	20.6	166.5	166.7	-0.1	557.77	16000	74.76
2101	0.036	0.56	2.33	22.8	0.16	64.6	94.2	90.5	3.9	135.72	4700	95.85
2102	0.024	0.99	2.54	55.2	0.53	52.9	107.2	112.2	-4.7	209.8	7400	95.13
2103	0.02	1.26	2.42	36.4	0.24	46.6	91.3	86.9	4.8	116.69	4900	94.7
2108	0.005	0.48	0.93	60	17.5	54.8	100	134	-34.0	670.98	9600	77.88
2113	0.015	0.33	1.13	122.5	17.3	51.8	153	193	-26.1	131.65	33000	27.42
2115	0.01	0.85	1.2	550	60.8	51	462	664	-43.7	84.8	32000	6.19
2118	0.003	0.53	0.93	175	32.5	53.3	128	212	-65.6	234.47	27000	6.44
2277	0.003	0.25	11	97.5	21.8	48.8	143.5	179	-24.7	486.34	26000	24.87
2280	0.003	0.53	1.53	75	14.5	42.5	59	134	-127.1	468.96	21000	35.32
2284	0.015	0.85	1.63	112.5	27.8	48.3	150	191	-27.3	330.29	33000	11.1
2330	0.072	3.32	6.24	544.6	12.26	8.1	540.9	575.9	-6.5	145.31	16000	37.51
2331	0.126	5.84	8.63	522.1	41.75	84.1	690.3	662.4	4.0	140.92	28000	6.03
2334	0.003	1.26	3.37	137.4	3.2	101.3	210.9	246.5	-16.9	153.84	21000	16.2
2335	0.072	3	5.74	308.6	16.66	13.5	330.1	347.5	-5.3	409.41	26000	7.9
2369	0.003	3.74	7.87	455.1	26.23	148.4	658.8	621.9	5.6	91.64	17000	30.46
2370	0.125	1.3	1.3	525	32	39.5	356	599	-68.3	104.07	27000	9.4
2371	0.025	0.85	1.38	283	50	68.5	143.5	478	-233.1	199.55	24000	11.55
2373	0.005	0.38	0.5	45	12.3	52	64.5	110	-70.5	287.29	18000	11.62
113	0.003	0.5	8.7	90	9.08	65.9	188	174.5	7.2	284.8		

EXCHANGE EXP

SAMPLE	INTERSTITIAL ZINC UG/L	BQ/2ML	MEAN OF A AND B	LOG (ZN-65) IN FRACTION	SPECIFIC ACTIVITY BQ/UG	MEAN OF A AND B	SUM OF CHEMICAL FRACTIONS UG/G
1A	82	1.93	1.93	0.285557309	11.8	11.8	473
1B	61						480
2A	111		2.48	0.3944516808		16.8	420
2B	74	2.48			16.8		380
3A	53	1.56	1.56	0.1931245984	14.7	14.7	438
3B	61						413
4A	54	2.54	1.48	0.1687920203	19.8	11.9	435
4B	51	0.41			4.0		404
5A	64	1.62	1.07	0.0273496078	12.7	9.5	416
5B	40	0.51			6.4		398
6A	47	0.84	0.70	-0.15490196	8.9	7.0	415
6B	56	0.56			5.0		390
7A	58						431
7B	44						381
8A	36						412
8B	51						390
9A	124	1.65	1.88	0.2730012721	6.7	7.6	411
9B	123	2.1			8.5		382
10A	198	2.59	1.70	0.2304489214	6.5	4.3	404
10B	189	0.81			2.1		378
11A	151	3.3	2.59	0.4132997641	10.9	8.9	394
11B	138	1.88			6.8		370

**QH
90.8
.B46
A53
1988**

Availability of zinc to benthic
organisms from sediment
fractions / Andrews, Daniel.
79573